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# TECHNICAL PROGRESS REVIEW

## REACTOR FUEL PROCESSING

PREPARED BY ARGONNE NATIONAL LABORATORY FOR THE U. S. ATOMIC ENERGY COMMISSION

FEBRUARY 1958

VOLUME I

NUMBER 1

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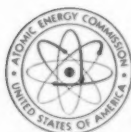
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# REACTOR FUEL PROCESSING

*a review of recent developments prepared by*

ARGONNE NATIONAL LABORATORY

FEBRUARY 1958    VOLUME I    NUMBER I





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## *foreword*

This quarterly review of Reactor Fuel Processing has been prepared at the request of the Division of Information Services of the United States Atomic Energy Commission (USAEC). It is intended as an aid to those interested in keeping abreast of progress in this field.

Since this is the first of this series, some introductory material, not necessarily new, is included. In each review it is intended to cover those particular subjects in which significant advances have been made. The review does not purport to abstract all the literature published on this subject during the quarter, rather it is the intention to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results where given are the opinions of the editors who are personnel of the Chemical Engineering Division of Argonne National Laboratory. The reader is urged to consult the original reference to obtain background material and the interpretation of the authors.

In May of this year a Symposium on the Reprocessing of Irradiated Fuels was conducted at Brussels, Belgium, by the USAEC for the Centre d'Études pour les Applications de l'Énergie Nucléaire and for invited guests from the Organization for European Economic Cooperation nations. At this meeting nearly fifty papers were presented on all phases of chemical processing. They have been published in three volumes as Report TID-7534. These volumes represent a current assessment of the whole field and contain a more complete discussion of chemical processing, particularly on an unclassified basis, than has ever before been available in one place. Some of the material in TID-7534 is referred to in this review, but because of the importance of this document a complete list of the papers is included as an appendix to this report.

S. Lawroski  
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# REACTOR FUEL PROCESSING

## COMMERCIAL ASPECTS OF FUEL PROCESSING

The Atomic Energy Commission (AEC) announced on May 18, 1957, that it will pay from 30 to \$45/g for plutonium produced in private reactors between that date and July 1, 1962. The price will vary within this range depending upon the  $\text{Pu}^{240}$  content of the material (Table I-1). For the subsequent year until July 1,

Table I-1 AEC PRICE FOR PLUTONIUM PRODUCED IN PRIVATE REACTORS AS A FUNCTION OF  $\text{Pu}^{240}$  CONTENT\*

$\text{Pu}^{240}$ , %	Price, \$/g Pu
0.0	45.00
2.0	41.50
4.0	38.00
6.0	34.50
8.0	31.00
8.6 and over	30.00

\*Prices valid until July 1, 1962. Between July 1, 1962, and July 1, 1963, the price will be a flat \$30/g.

1963, the price will be a flat \$30/g. The earlier price had been \$12/g, but this was rescinded last fall. The \$30/g price is approximately equivalent to a raw material fuel cost of 5 mills/kw-hr and the \$12/g figure to 2 mills/kw-hr. Although these high prices are attractive from a processor's view, he must appreciate the fact that they are artificial and apply to a limited period during which only a modest quantity of materials will be available for processing.

The Commission announced on Feb. 18, 1957, that spent fuel from private power reactors would be reprocessed in government-owned plants at firm charges that would be subject to cancellation on a 12-month notice upon determination that reprocessing services were commercially available at a reasonable price.\*

\*Published in U. S. Federal Register, Mar. 12, 1957.

These costs are based on a design for a hypothetical plant running at full capacity for 300 days/year. It assumes solvent-extraction processing of various fuels that are treated with one of several head-end processes. The derivation of the capital cost of this plant, \$20,500,000, is shown in Table I-2, and the annual operating cost is shown in Table I-3. From Table I-3, a standard daily charge is calculated (Table I-4), and the processing charge for several typical fuels is shown in Table I-5.

Table I-2 CAPITAL COST SUMMARY FOR MULTI-PURPOSE CHEMICAL-PROCESSING PLANT

Labor and materials:	
Canal and equipment	\$750,000
Mechanical treating equipment	540,000
Chemical make-up and storage	270,000
Radioactive off-gas facility	900,000
Prorated utilities	770,000
Waste evaporator	75,000
Liquid-liquid extraction	1,605,000
Enriched Zircex dissolution*	480,000
Low-enrichment Zircex dissolution	150,000
Enriched Darex dissolution†	150,000
Low-enrichment Darex dissolution	360,000
$\text{H}_2\text{SO}_4\text{-HNO}_3\text{-HF}$ dissolution	1,260,000
HCl distillation	900,000
Solids separation	180,000
Buildings	4,837,000
Total labor and materials	\$13,227,000
Construction overhead and fee (40%)	5,291,000
Subtotal	\$18,518,000
Engineering and inspection (10%)	1,852,000
Subtotal	\$20,370,000
Product containers	200,000
Grand total capital	\$20,570,000

\*A dissolution procedure for zirconium-uranium alloys in which HCl gas is used to form volatile  $\text{ZrCl}_4$  and nonvolatile  $\text{UCl}_5$  which is dissolved in nitric acid.

†A dissolution procedure for stainless-steel fuels using dilute aqua regia.

It should be emphasized that the significant cost is not that figured on a dollars per kilogram basis but rather the cost determined on the basis of dollars per megawatt day of heat or

Table I-3 ANNUAL OPERATING AND WASTE-STORAGE COSTS FOR CONCEPTUAL MULTI-PURPOSE CHEMICAL-PROCESSING PLANT

Direct operating personnel and supervision (53 @ \$7,200)	\$382,000
Maintenance	130,000
Supplies	170,000
Analytical services	102,000
Health physics	36,000
Services:	
Steam	72,000
Air	8,000
Electricity	22,000
Water	20,000
Subtotal	\$942,000
Overhead and other	467,000
Total operating	\$1,409,000
Waste storage	527,000
Total operating and waste	\$1,936,000

Table I-4 DERIVATION OF AEC STANDARD DAILY CHEMICAL-PROCESSING CHARGE

Annual depreciation (@10%)	\$2,057,000
Annual operating and waste storage	1,936,000
Subtotal	\$3,993,000
Annual AEC overhead	599,000
Total annual costs	\$4,592,000
Standard AEC daily charge (300 days/year)	\$15,300

Table I-5 PROCESSING CHARGE FOR SEVERAL TYPICAL FUELS

	Plate assemblies*	Pin assemblies†	UO <sub>2</sub> pellets‡
Assumed quantity, kg U	12	5,475	22,000
Processing rate, kg U/day	44	150	1,000
Processing time, days	0.3	36.5	22
Turnaround time, days	3	8	8
Total plant time, days	3.3	44.5	30
Processing charge, \$	50,500	681,000	459,000
Unit charge, \$/kg total U	4,200§	124	21

\*90 per cent enriched uranium as a zirconium alloy, zirconium clad.

†27 per cent enriched uranium as a 10 per cent molybdenum alloy, zirconium clad; stainless-steel structural material.

‡2.5 per cent enriched in stainless-steel tubular assemblies.

§This high unit cost is due to the fact that the ratio of operating to turnaround time is low because of the limited quantity of this type of fuel processed.

electrical energy produced. This will be determined by the degree of burn-up obtained from the fuel elements as well as the value of any

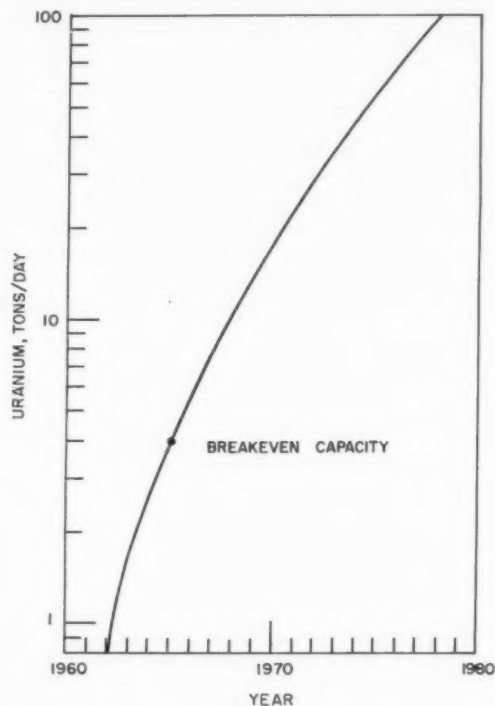


Fig. 1—Reprocessing load vs time. Breakeven capacity fixes time of first central unit.

bred material that can be recovered from the processed fuel. On this basis these fuel-processing charges for the reactors studied thus far by the power industry groups and the Commission appear to be in the range of 0.2 to 2 mills/kw-hr. These figures do not include the further steps in the fuel cycle in which the nitrate products are converted to a usable form, e.g., metal. A 1 per cent loss going from irradiated fuel to final product has been assumed and charged.

It has been predicted<sup>1</sup> that a private fuel-processing plant will be feasible about 1965. These estimates are based on a number of assumptions:

1. That nuclear electric power will sell for 8 mills/kw-hr
2. That the power reactor used will have a capital investment of \$250/kw of installed electrical capacity
3. That the fuel will operate at a 4000-Mwd heat per metric ton uranium irradiation level

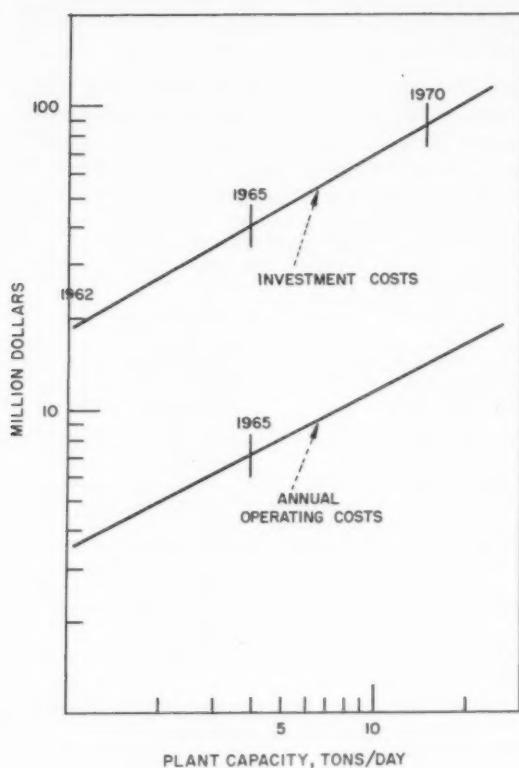


Fig. 2—Process cost breakdown.

4. That the thermal efficiency will be 25 per cent.

On these assumptions the total fuel recycle cost cannot exceed \$17/kg of uranium. Since the fuel recycle cost includes fuel fabrication, shipping, and storage, as well as fuel processing, it is also arbitrarily assumed that the processing charge cannot exceed \$8/kg of uranium or about 0.4 mill/kw-hr of electricity.

Chemical-processing costs are most sensitive to plant throughput. Accordingly, the earliest date when it will be possible to build a spent-fuel processing plant and operate it with an economically acceptable charge will be determined by the growth of the nuclear power industry. Using estimates of the McKinney Panel, the daily reprocessing capacity required is shown in Fig. 1. Military reactor demands are not included in this figure. Figure 2 shows the estimated relation between reprocessing plant capacity and required capital investment for chemical plants capable of processing the diversified power re-

actor fuels up to 2 per cent enriched uranium. These estimates are based on conceptual design studies rather than actual experience and therefore may be in error. It is significant that estimated capital investments of roughly \$20 million, \$40 million, and \$80 million will be required to service the nuclear power industry of 1962, 1965, and 1967, respectively.

Operating costs for this hypothetical plant are also shown in Fig. 2. Figure 3 presents expected fuel decontamination costs obtained from the data of Fig. 2 as a function of plant capacity. On the premise that fuel recovery should be accomplished at a cost of 0.4 mill/kw-hr, a 4 ton/day plant is required to break even. Sufficient fuel to keep this plant on stream 100 per cent of the time should become available in 1965 (see

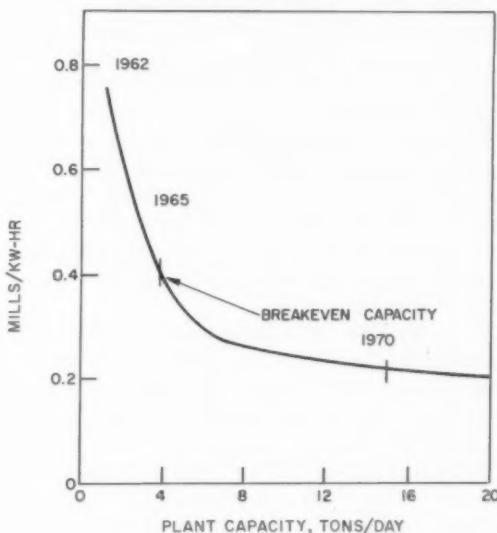


Fig. 3—Recovery cost vs capacity.

Fig. 1). This conclusion is based on McKinney estimates; actual performance to date is closer to Atomic Industrial Forum minimum figures which would make this date five to ten years later. This conclusion makes no allowance for costs incurred in fuel shipping and storage, fuel inventory, plant downtime, or for profit. Bruce concludes that a central processing plant is a necessity, and a rough survey indicates that the optimum location for the first plant would be in the vicinity of Indianapolis, Ind.

### Reference

1. F. R. Bruce, *Chemical Engineering*, 64(7): 202 (July 1957).

## PREPARATION OF FUELS FOR PROCESSING

The increasing number of proposed reactor designs involves an increasingly large number of fuel types, approximately 30 at the present time. Before actual processing begins, most fuels require storage, mechanical or chemical disassembly of the element, dissolution of the fuel proper, and perhaps a chemical pretreatment prior to processing.

### Storage

Storage of an irradiated fuel element may be required prior to processing in order to reduce activity levels to a point tolerable in the process. This is generally true of solvent-extraction plants. If very low radioactivity level of the product is required, storage may be necessary in any case to allow decay of transmutation isotopes.

The cost of decay storage consists of three types of charges: (1) the cost of storage space, (2) the use charge for any fissionable material leased from the AEC, and (3) an inventory cost for working capital tied up in fissionable material leased from the AEC or awaiting transfer to a customer.

To determine the total cost, it is necessary to define (1) the cost of the space and its operation, (2) the base charge\* for holding the fuel material,<sup>1</sup> and (3) the length of time the material will be held.

In the determination of an optimum fuel cycle, storage costs play an important part. The storage cost will be a function of reactor and reactor fuel type and of the processing scheme used.

Ullman and Arnold<sup>2</sup> have examined this problem for the two reactor types shown in Table II-1.

Various transmutation isotopes involve different storage requirements. These are summarized in Table II-2. For  $U^{235}$  fission the chief transmutation isotope is  $U^{237}$ . The  $U^{237}$  problem

can be reduced somewhat if, upon each pass, some of the  $U^{236}$  is removed in a gaseous diffusion plant. If, e.g., 25 per cent of the  $U^{236}$  were removed each time, cooling times of 30 to 40 days less would be required.

Table II-1 COMPARISON OF FUEL STORAGE FOR TWO REACTORS

	One-region reactor	Two-region reactor
Enrichment	2%	Core, 90%; depleted blanket
Irradiation level	3000 Mwd/ton	3000 Mwd/ton (equivalent)
Irradiation time	50 days	Core, 42 days; blanket, 250 days
Uranium loading	10 tons	Core, 85 kg; blanket, 50 tons
Flux (thermal)	$7.5 \times 10^{13}$ neutrons/(cm <sup>2</sup> )(sec)	Core, $1.5 \times 10^{14}$ neutrons/(cm <sup>2</sup> )(sec); blanket, $1.5 \times 10^{13}$
Specific power	60 Mw/ton	Core, 6 Mw/kg $U^{235}$ ; blanket, 1.8 Mw/ton depleted U
Decay time*	123 days	Core, 150 days; blanket, 107 days

\* To give a product that reads 20 mr/hr at 1 ft.

Table II-2 STORAGE REQUIREMENTS FOR SEVERAL TRANSMUTATION ISOTOPES

$Np^{239}$ in $Pu^{239}$	1-month decay of fuel or recover $Np^{239}$
$U^{237}$ in $U^{235}$	120-day decay of fuel or remote refabrication
$Pa^{233}$ in $U^{233}$	1-year decay of fuel or waste or recover $Pa^{233}$
$U^{232}$ in $U^{233}$	Repurify periodically to remove $U^{232}$ daughters
$Th^{234}$ in $Th^{232}$	1-year decay of fuel or product or increase refabrication cost
$Th^{228}$ in $Th^{232}$	60-day decay of fuel or increase refabrication cost

### Dissolution

After the fuel element is stored, it requires disassembly, which may be done mechanically, chemically, or by a combination of these methods. The fuel proper must then be dissolved. The variety of fuel types under consideration makes this problem more difficult.

Efforts are being made to find ways of handling all or most of these different elements in existing solvent-extraction plants. A breakdown of fuels (presented some time ago) into cate-

\* Schedule of Base Charges for Materials Sold or Leased by AEC for Use in Private Atomic Energy Development, Jan. 5, 1955.

gories and the methods necessary to prepare them for solvent extraction<sup>3</sup> are given in Table II-3.

than 0.1 per cent of the uranium is volatilized. The uranium that is converted to the chloride can be dissolved in water or nitric acid, the

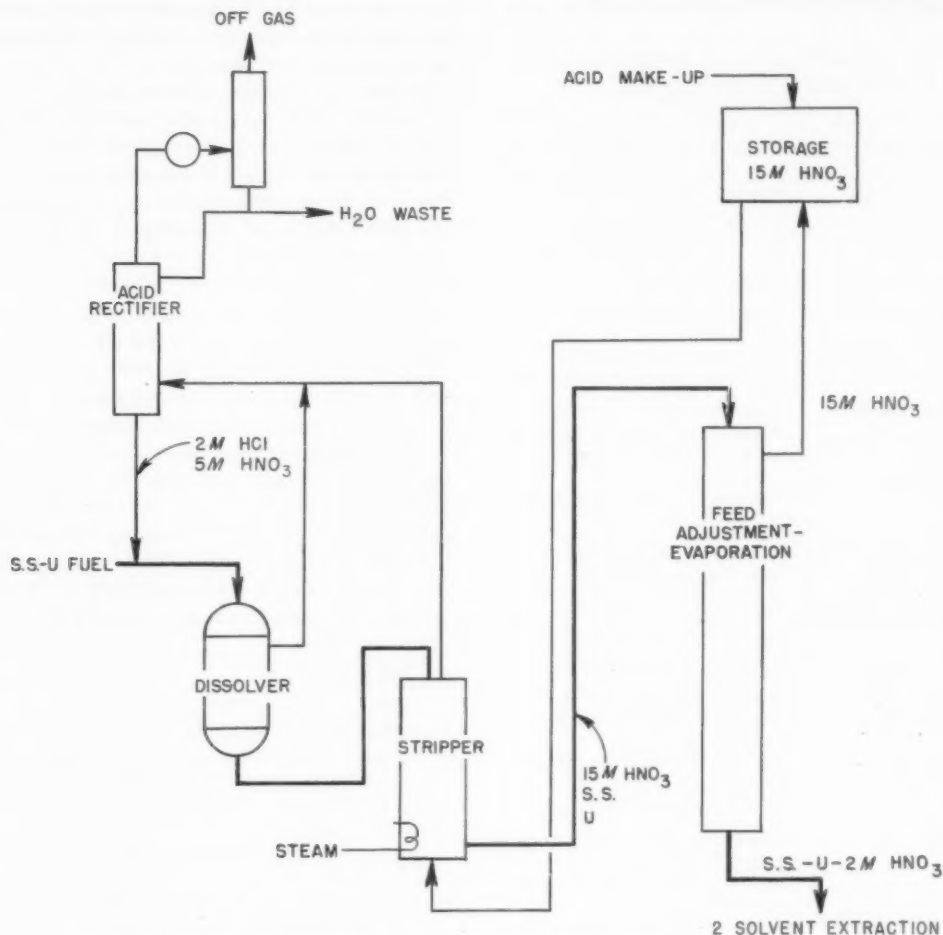


Fig. 4—Flow sheet for processing stainless-steel fuels by the use of dilute aqua regia (often referred to as Darex process).

Several methods being studied for handling fuels not soluble in nitric acid are worthy of mention. The reaction of HCl gas with zirconium at elevated temperatures to form volatile zirconium chloride ( $ZrCl_4$ ) can be used to convert zirconium metal to volatile zirconium chloride and quantitatively remove zirconium from Zircaloy-2\* or zirconium-uranium alloys at acceptable rates (0.3 to 0.7 mg/(min)(cm<sup>2</sup>)).<sup>4</sup> Less

chloride removed by distillation, and the uranium recovered by solvent extraction. This process is sometimes referred to as the "Zircex process."

The incorporation of such materials as stainless steel, zirconium, niobium, molybdenum, and silicon in fuel alloys necessitates the use of corrosive dissolving mediums, e.g., hydrofluoric acid, sulfuric acid, and dilute aqua regia. This has led to the concept of confining the corrosive reagents to head-end equipment that can be constructed of more costly corrosion-resistant materials.

\* A zirconium alloy containing 1.5 wt. % tin, 0.15 wt. % Fe, 0.10 wt. % Cr, and 0.05 wt. % Ni.

Development work<sup>3,5</sup> indicates that a dilute aqua regia process may have promise for processing all types of stainless-steel fuels (see Fig. 4). The head-end equipment in this

Table II-3 CLASSIFICATION OF HETEROGENEOUS FUELS FOR INTRODUCTION INTO SOLVENT-EXTRACTION PLANTS

Classification	Principles
Enriched (~90% U <sup>235</sup> ) UO <sub>2</sub> -stainless steel	Requires criticality control No Pu recovery Not directly HNO <sub>3</sub> soluble High inert content (>90 wt. % stainless steel)
Enriched (~90% U <sup>235</sup> ) U-Zr alloy	Requires criticality control No Pu recovery Not directly HNO <sub>3</sub> soluble High inert content (>90 wt. % Zr)
Enriched (~90% U <sup>235</sup> ) UO <sub>2</sub> , UC <sub>2</sub> , or U-Al alloy, Pu-Al alloy, or Pu	Requires criticality control No Pu recovery (enriched U case) Soluble in HNO <sub>3</sub> catalyzed by Hg or HF High inert content (~96% Al for U-Al alloy)
Enriched (~20% U <sup>235</sup> ) U metal, UO <sub>2</sub> , or U alloyed with Zr, Nb, Mo, or Si, etc.	Requires criticality control Requires Pu recovery Soluble in HNO <sub>3</sub> (except for Zr alloys*) Low inert content (<15% Zr, etc.)
Natural or slightly enriched (~2% U <sup>235</sup> ) U metal, UO <sub>2</sub> , or U alloyed with Zr, Nb, Mo, or Si, etc.	Essentially no criticality control Requires Pu recovery Soluble in HNO <sub>3</sub> (except for Zr alloys*) Low inert content (<15% Zr, etc.)
Thorium	Essentially no criticality control Requires U <sup>233</sup> recovery Soluble in HNO <sub>3</sub> catalyzed by HF No inert content

\* Zr-U alloys are explosive in pure nitric acid.

case would be lined with titanium which is reported<sup>6</sup> to have a corrosion rate of 5 mils/year in dilute aqua regia.

Many of the alloys of uranium with less than 15 wt. % niobium, molybdenum, or silicon are

soluble in nitric acid or dilute aqua regia at acceptable rates and leave less than 1.0 per cent uranium in insoluble residues. The direct dissolution of zirconium alloys is not practical because of the explosive powders that form on the dissolving surfaces.

Dissolving zirconium and stainless-steel fuels in molten aluminum, zinc, or magnesium at 800 to 1000°C has been studied as a means of converting them to a nitric acid soluble form.<sup>3</sup> About 6 hr is required to alloy completely a 100-mil sample of Zircaloy-2 at 850°C with zinc using a mole ratio of zinc to zirconium of 8.0. The principal advantage of this system for zirconium and stainless-steel fuels is the elimination of the use of corrosive ions such as fluoride. Disadvantages include high-temperature operations, addition of inerts to the system, and excessive uranium losses.

The feasibility of dissolution of Zircaloy-2 cladding in ammonium fluoride solutions has also been shown.<sup>7</sup> In experiments involving dissolution of Zircaloy-2 in boiling 6M ammonium fluoride, a reaction time of 1 hr is sufficient for the dissolution of a thickness of 30 mils to a final zirconium concentration of 1M.

## References

1. "AEC Manual," Billing and Collection Procedures, Chap. 1704 (available for inspection in the public documents room, USAEC, Washington).
2. J. W. Ullmann and E. D. Arnold, *Nucleonics*, 15 (6): 80 (1957).
3. R. E. Blanco, *Nuclear Science and Engineering*, 1: 409 (1956).
4. R. E. Blanco et al., ORNL-2228, Feb. 13, 1957, p. 9. (Confidential AEC report.)
5. R. E. Blanco, Symposium on the Reprocessing of Irradiated Fuels, Book 1, Brussels, Belgium, TID-7534, May 20, 1957, pp. 251-261. (Unclassified AEC report.)
6. C. E. Hutchinson and P. H. Permor, *Corrosion*, 5: 319 (1949).
7. J. L. Swanson, HW-49633, Apr. 15, 1957. (Confidential AEC report.)



## FUEL-PROCESSING RESEARCH AND DEVELOPMENT

In this section an attempt will be made to cover new work on existing separations processes and on proposed processes. The general areas covered will be solvent extraction, precipitation, ion exchange, volatility and pyrometallurgical processing, processing for homogeneous reactor systems, corrosion, and instrument and equipment development. It is not expected that each subject will appear in each review.

eral years to recover and purify uranium and plutonium from irradiated fuels. Descriptions of the two major processes (Redox and Purex) as well as descriptions of similar solvent-extraction processes modified to handle enriched fuels and fuels containing various alloying agents such as zirconium and stainless steel have been published in the open literature (see Appendix).<sup>1,2</sup>

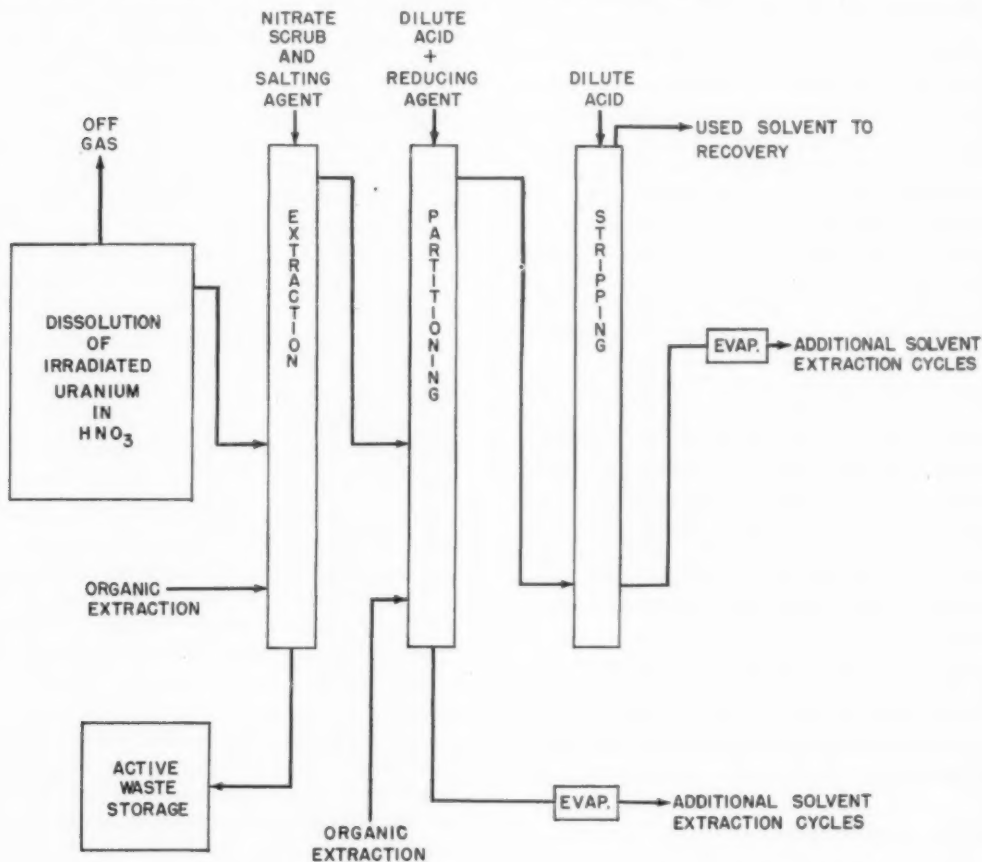


Fig. 5—Generalized solvent-extraction flow sheet.

### Solvent Extraction

Continuous solvent-extraction processes have been developed and used successfully for sev-

A generalized solvent-extraction flow sheet is shown in Fig. 5. It is typical for the Redox process, which is characterized by the use of hexone (methyl isobutyl ketone) as the solvent.

This flow sheet also applies to the Purex process, which is characterized by the use of tributyl phosphate (TBP) diluted with hydrocarbon diluent, but sometimes the general flow sheet for the Purex process differs in that partitioning of the uranium and plutonium is delayed to the second cycle, the first cycle being a co-decontamination cycle. In both processes the separation of plutonium from uranium is based on the high organic solvent extractability of plutonium in the oxidized state (IV or VI valence state) and the relative inextractability of plutonium in the reduced trivalent state. Both processes provide very good separation of plutonium and uranium and excellent decontamination from fission products. Because the Purex process can and does use a volatile and recoverable salting agent ( $\text{HNO}_3$ ), it is superior to Redox in regard to waste volumes from unalloyed fuels such as natural uranium.

Packed columns have been successfully employed for the Redox process; pulsed columns and mixer-settlers have been used with the Purex process. All are proving satisfactory in remotely operated high throughput processing plants.

Space limitations prevent detailed descriptions of these and other processes. The Thorex process used for the separation of uranium, thorium, and protactinium is basically similar. Processes for enriched uranium fuels are also similar. With these latter fuels the quantity of plutonium encountered is so small that it is discarded, and therefore the partitioning columns and later plutonium purification cycles are not required.

With this brief introduction it is the intent to present new material in three categories: (1) process improvements, (2) accommodation of new fuels, and (3) plant and equipment design and operation.

### Process Modifications

Attention is initially called to developments in the Redox and Purex processes. One is the backcycling of aqueous wastes which serves to reduce to some extent the waste volumes, i.e., a low-activity third-cycle uranium waste can be concentrated and used as a portion of the scrub solution for the second cycle, etc. (see pp. 27-31).

Other developments have stemmed from a desire to operate the interface in an extraction

column near the bottom or aqueous-waste take-off point.<sup>3</sup> This is considered advantageous from the standpoint of improving decontamination. The interface accumulates foreign solid materials, which in turn accumulate high levels of radioactivity. Operation with the interface at the top near the product takeoff jeopardizes decontamination because of possible carryover of this foreign material into the solvent product stream.

In the Purex process it has been found that operation with the interface at the bottom (organic phase continuous) using stainless-steel sieve plates is not so efficient as operation with the interface at the top (aqueous phase continuous). This has led to a development of sieve-plate cartridges suitable for operation with the organic phase continuous. A satisfactory extraction-section cartridge is composed of stainless-steel nozzle plates having  $\frac{3}{16}$ -in.-diameter holes, 23 per cent free area, 0.04-in.-deep nozzles pointing downward, and a 2-in. plate spacing. The most promising scrub-section cartridge found is a mixed cartridge containing alternate pairs of fluorothene and stainless-steel sieve plates. Use of alternate materials, one of which (the fluorothene) is wet by the organic and the other by the aqueous phase, changes the continuous phase so that the liquid in a scrub section consists of alternate layers of organic-phase-continuous and aqueous-phase-continuous dispersions.

It has also been found that the decontamination performance of the Purex process can be improved by operation of scrubbing sections at temperatures of about 50°C instead of at room temperature.

*1. Substitution of Ion Exchange for Second Plutonium Cycle.* A process is being studied in which an ion-exchange cycle<sup>4</sup> is substituted for the second Purex plutonium cycle. In either case (i.e., second extraction or ion-exchange cycle), the plutonium product must be further purified by an additional ion-exchange cycle and subsequently concentrated by precipitation as the peroxide. When two ion-exchange cycles are employed, great dependence is placed on the peroxide precipitation step to provide additional rare-earth decontamination. No economic evaluation has been carried out to determine the merit of two ion-exchange cycles, rather than one each of solvent extraction and ion exchange.



## 2. Low-acid First-cycle Purex Flow Sheet.

A low-acid first-cycle Purex flow sheet<sup>5</sup> was designed by optimization of several parameters to give the minimum amount of waste consistent with low product loss and adequate decontamination. A 50 to 70 per cent reduction in the first-cycle aqueous waste is claimed without affecting decontamination, product recovery, or system stability by taking advantage of the extractability and reflux of nitric acid in TBP systems.

**3. Plutonium Reflux Process.** A reflux flow sheet<sup>6</sup> has been developed and demonstrated on a semiworks scale for plutonium concentration, recovery, and purification which enables the production of a concentrated plutonium product (up to 110 g/liter) from feed sources (scrap material and solvent-extraction product solutions) that vary widely in plutonium content and chemical composition. The solvent is 15 vol. % TBP in a carbon tetrachloride diluent. The plutonium is in the IV or VI valence state, but control of the particular valence state of plutonium is not necessary since even that in the III state is converted to Pu(IV) under the acid and salt conditions of the extraction column. Semiworks operation of this process in pulsed, perforated plate columns was distinguished by the general stability of the system under widely varying feed conditions.

The advantages of a reflux process are that it eliminates subsequent concentration steps and that it is flexible in its ability to handle widely different feeds while producing a uniform product. The disadvantages are that the greater plutonium process inventory requires a criticality control system and somewhat greater extraction efficiencies because of the handling of concentrated plutonium solutions. Despite these disadvantages, product refluxing may be considered an efficient and practical technique for providing concentrated plutonium solutions.

**4. Neptunium Recovery.** The isolation of decontaminated neptunium from either the Redox or Purex process<sup>7</sup> is believed to be feasible. In the Redox process the neptunium and plutonium could be co-decontaminated by utilizing the Argonne National Laboratory (ANL) acid flow sheet. Subsequently they could be separated by ion exchange.

In Purex the neptunium could be isolated by anion exchange from the concentrated second-

cycle wastes as they are backcycled to the first extraction column. Two alternate flow sheets are currently being studied for the assured extraction of neptunium in the first cycle. In the first alternate, uranium, plutonium, and neptunium are coextracted, the oxidation potential being achieved by the use of manganese dioxide or a nitrate-nitrite system. In the second alternate, Np(IV) and U(VI) are coextracted using ferrous ion as a plutonium reductant. This keeps the plutonium in the fission-product waste stream, from which it is subsequently extracted in a separate column for separate decontamination. This flow sheet is expected to yield somewhat poorer decontamination than the first alternate, necessitating more reliance on tail-end decontamination steps.

Process modifications were not found which would route the neptunium with Redox uranium product for subsequent recovery from the fluorination ash. This would be possible in the Purex process, but the process conditions necessary would tend to reduce the decontamination obtainable, and could therefore jeopardize plans currently being activated for operation of a two-cycle flow sheet incorporating a waste backcycle.

Flow sheets have been developed for the solvent-extraction recovery of uranium and Np<sup>237</sup> from special highly irradiated Materials Testing Reactor (MTR) fuel elements and from nonvolatile fluoride residues from the Oak Ridge Gaseous Diffusion Plant.<sup>8</sup> In both cases the material containing the neptunium and uranium is dissolved and digested to inactivate emulsion-forming impurities; the neptunium and uranium are then extracted with TBP solvent using aluminum nitrate (scrubbed free of fission products and/or ionic contaminants) as the primary salting agent, and are finally separated and recovered by selective stripping with nitric acid.

## Accommodation of New Fuels

Conventional solvent-extraction processes have proved very satisfactory for fuels containing uranium and aluminum (as a cladding or alloying material) as the basic components. However, there has been increasing interest and use of other fuel-element types that are clad with or alloyed with materials such as zirconium, stainless steel, and niobium to provide

increased corrosion resistance or radiation stability.

These fuels are not readily soluble in nitric acid, and their recovery using conventional solvent-extraction processes has necessitated the development of special head-end processes that place the fuel in a nitrate solution. These head-end processes that enable the accommodation of many fuels in presently developed solvent-extraction processes have been described in the preceding section.

1. *Studies of Solvent Radiation Damage.* An important factor in reprocessing nuclear reactor fuels by solvent extraction is the radiation damage<sup>9</sup> to the process reagents (principally the organic solvents), especially in the case of short-cooled fuels where the fission-product radiation is very intense. In TBP extraction systems, which employ TBP diluted by a hydrocarbon diluent, noticeable solvent radiation damage, as indicated by a detectable drop in decontamination, occurs at radiation doses as low as 0.5 watt-hr/liter. Significant radiation damage effects occur at exposures of 20 watt-hr/liter, as shown by retention in the solvent (unstrippability) of plutonium and uranium, as well as by a decrease in decontamination. Little, however, is known about radiation-induced emulsifiers that would impair or possibly prevent first-cycle operation.

Radiation dosages of the order of 10 watt-hr/liter would be expected for short-cooled fuels. Process modifications that would reduce radiation damage are feed dilution and reduction of residence time in the contactors.

2. *Processing of Oxide Fuels.* Studies are under way<sup>10,11</sup> to determine the adaptability of the Purex process to the recovery of Fast Oxide Breeder fuel (a mixture of plutonium and uranium oxides). The most important factor is radiation damage to the solvent which results in substantially increased extraction of zirconium.

3. *Application of Solvent Extraction to Processing Uranium Ores.* Solvent extraction offers a new method of processing sulfate leach liquors resulting from the leaching of crushed and ground uranium ores.<sup>12</sup> Two general classes of organic solvents have proved economically suitable: (1) the organic phosphoric acids and (2) the alkyl amines. Good performance of a process employing a solvent of the first type,

dodecyl phosphoric acid, was demonstrated in a 10 gal/min pilot plant operated by the Vitro Uranium Corp. As a result, Vitro is converting its Salt Lake City mill to this process.

It was concluded that the inherent flexibility of solvent extraction and the wide choice of reagents possible offer a large number of combinations for purification of uranium from ores to final high-grade concentrates.

## Plant and Equipment Design and Operation

1. *Plant Design—Nuclear Safety.* Since spent reactor fuels contain fissionable material, adequate controls must be included in the design of reprocessing plants to prevent accumulation of sufficient material to support a nuclear chain reaction. This may be accomplished by one or a combination of several methods: (1) geometry, (2) batch-size limits, (3) solution concentration limits, and (4) neutron absorbers.

Critical mass data for a variety of conditions have been collected.<sup>13-15</sup>

It is difficult to write a set of nuclear safety rules that apply to all plant-processing conditions. For reprocessing of spent reactor fuels where a great variety of techniques and conditions may be represented, over-all regulations are likely to be misapplied. Blind applications of general rules can work in two directions. Misapplication in one direction can lead to criticality accidents that are dangerous to both life and property. Misapplication in the opposite direction with insufficient attention to extenuating conditions may lead to unnecessary expense in both the construction and operation of large-volume processing plants. Therefore it is necessary to understand the principles of reactor physics as well as the plant-processing conditions involved to ensure the proper application of these rules as well as to determine criticality conditions for process steps that cannot be covered by general rules.

2. *Equipment Design—Dual-clone Liquid Separator.* Hydraulic cyclones or hydroclones have been considered to remove micron-sized particles from aqueous homogeneous reactor fuel solutions.<sup>16</sup> Removal of such particles required hydroclones of less than 1 in. diameter resulting in units with very small fluid holdup volumes. To minimize radiation damage to solvents used in processing short-cooled reactor fuels, it was proposed<sup>17</sup> that high-speed

mixing and settling might be achieved by replacing the gravity settling chamber with a hydroclone and the mixing chamber with a jet or centrifugal pump.

Preliminary tests have shown that complete phase separations are not possible with a single hydroclone. The performance of a hydroclone is such that water-free solvent is produced from a solvent-water mixture only at the expense of a very poor separation of solvent from water. The analogous situation exists for solvent-free water production. To overcome this difficulty, two hydroclones were arranged so that each operated for clarification of a single phase. The underflow from the first hydroclone is fed to the second, and the overflow from the second is recycled to the feed. This arrangement (dual-clone separation) makes possible essentially complete phase separation and reduces the flow-control problem.

Experimentation is continuing with various pump systems, flow-control methods, and equipment configurations. The scheme has not yet been reduced to practice.

**3. Ultrasonic Liquid-Liquid Extractions.** The concept of ultrasonic emulsification followed by ultrasonic emulsion breaking as a contacting method for solvent extraction was explored<sup>18</sup> on a laboratory scale with a number of liquid systems. Continuous ultrasonic emulsification was demonstrated as a satisfactory contacting method, and ultrasonic emulsion breaking was accomplished on a continuous basis.

Diameters of the dispersed droplets initially formed by ultrasonic emulsification were generally in the region of 95 per cent less than  $2\ \mu$ , although dependence on flow rate was indicated. Droplet size requirements estimated from evaluation of Fick's diffusion law suggest that flow rates could probably be increased to such an extent that the particle diameter might be as large as 100 to 200  $\mu$ , and extraction could still be attained within a contact time of the order of 0.1 to 0.01 sec. This is in contrast to droplets of the order of 300 to 2000  $\mu$  normally attained in spray and other type extraction towers. Whereas very stable emulsions were formed in systems containing no acid, the acidic systems formed emulsions that broke rapidly into very dilute (approximately 1 per cent) water-in-oil and oil-in-water emulsions. If the situation permits the carry-over of these dilute emulsions to the subsequent stage, the

necessity for interstage clarification is obviated, and ultrasonic emulsion breaking could then be carried out only on the end-product streams.

Liquid-extraction systems that were studied included nitric acid-kerosene with water, acetic acid-kerosene with water, and uranyl nitrate-nitric acid extracted with TBP in kerosene.

A two-stage pilot-plant extraction unit incorporating ultrasonic mixer-settler type vessels was fabricated, and demonstration runs with the several liquid-liquid systems were satisfactorily completed. Extraction efficiencies of 99 per cent were obtained with acetic acid. Using the uranyl nitrate system, efficiencies of 85 to 90 per cent were obtained at total flow rates of 100 ml/min.

### *Ion Exchange*

A large number of chemical industries are currently using and planning further future applications for the unit operation known as ion exchange. Ion exchange may be defined as follows: "the reversible exchange of ions between a solid and a liquid in which there is no substantial change in the structure of the solid."<sup>19</sup> By this definition one of the ions must always be bound to the immobile solid and is therefore not carried away by the solution. This fact embodies the principal advantage of the process of ion exchange.

There are already numerous applications of ion exchange in the atomic energy industry. It has been used in the decontamination of dilute radioactive wastes, in concentration of uranium and plutonium products from solvent-extraction processes, and in other applications where concentration or decontamination of a dilute solution may be desired. In this section methods of isolation of plutonium and uranium, continuous countercurrent ion exchange, ion-exchange studies with polonium, and separation of americium from a rare-earth mixture (primarily lanthanum) will be discussed.

### *Isolation Processes*

Chemical processes<sup>20</sup> for the separation of fissionable material from fission products and other contaminants in discharged reactor fuel usually produce a dilute solution of the product in nitric acid. Before the fissionable material may be converted to the metal, it must be concentrated and further purified from residual

fission and corrosion products. Ion exchange is one of the best methods for such concentration and purification operations.

Ion-exchange processes have been developed which both concentrate the fissionable material and give additional separation from corrosion and fission products. The processes were developed specifically for the plutonium product

1. *Plutonium Isolation.* In the plutonium ion-exchange process, beta and gamma decontamination factors of about 3 and 5, respectively, are obtained. The ion-exchange step is particularly effective for zirconium and niobium decontamination, factors of 40 and 20, respectively, being obtained. The plutonium loss is only  $10^{-4}$  per cent, and the product is recovered

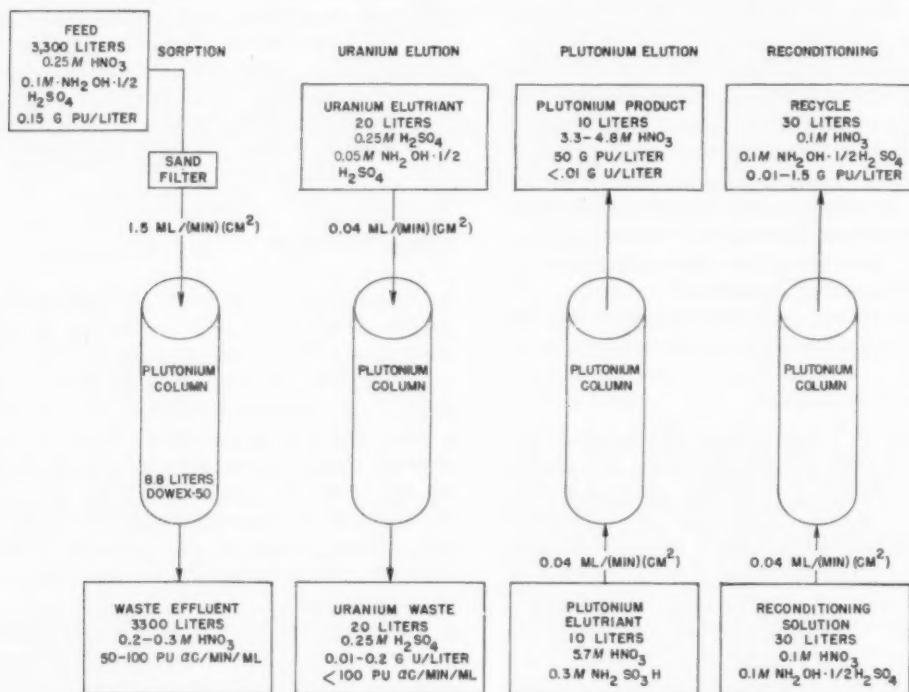


Fig. 6—Metal recovery plutonium isolation flow sheet.

from the Purex and Redox processes and for the uranium from the Thorex process. These two processes have been demonstrated on the pilot-plant and full-plant scale. There are also applications to plutonium and uranium isolation from other processes.

Cation-exchange isolation procedures are believed most applicable to the processing of dilute solutions containing less than 10 g of uranium or plutonium per liter and requiring little or no additional decontamination from fission products. If the product concentration in the feed is high or if appreciable separation from fission products is required, some other technique may be more advantageous.

at a concentration of 40 to 50 g/liter. If the product stream from the Purex process is used as feed, a plutonium concentration factor of about 250 is obtained. Dowex-50 resin (50 to 100 mesh, 12 per cent cross linkage) is used in this process. A flow sheet of the process is given in Fig. 6.

2. *Uranium Isolation.* Similarly  $U^{233}$  may be recovered from the product stream of the Thorex process by ion exchange. The principal impurities are thorium, protactinium, corrosion products, fission products, and aluminum. In the  $U^{233}$  ion-exchange process, gross beta and gamma decontamination factors of approximate-



ly 10 and 50, respectively, have been obtained. The loss is only  $10^{-3}$  per cent of the  $U^{233}$ , and the product is recovered at a concentration of about 140 g/liter. Dowex-50 resin (50 to 100 mesh, 8 per cent cross-linked) is used in this process.

### Separation of Americium from Rare Earths

Armstrong et al.<sup>21</sup> have reported on the separation of 4.5 g of americium from approximately 1 kg of light rare earths (primarily lanthanum) from a process fraction by ion exchange on a pilot-plant scale. The separation was achieved by chromatographic displacement of the mixture from Dowex-50 resin with 0.1 per cent ammonium citrate at pH 8 into hydrogen-form Dowex-50. The americium was collected into a narrow band and was eluted free from lanthanum but contained an equal weight of cerium. Two columns (6 and 2 in. diameter) were used in tandem. Use of a final column of much smaller diameter would have permitted a cleaner separation from cerium, but this was left for a laboratory-scale separation by a different process. Precipitation, which was observed in the columns during the first runs; was later avoided entirely by use of high flow rates, both initially and during the transfer between columns. No adverse effects were noted from ~15 curies of alpha activity.

### Continuous Countercurrent Ion Exchange

Data have been reported<sup>22</sup> for a continuous countercurrent ion-exchange column tested using the system Dowex-50W, calcium, and sodium forms. The ion-exchange column contained both loading (absorption) and stripping (regeneration) sections with the two sections separated by isolation zones of zero dynamic pressure differential. The resin was moved through the column in a dense bed countercurrent to liquid contamination and regeneration streams. Performance tests were carried out to show the feasibility of this type of column operation, to determine typical values of the equilibrium stage heights, and to measure the ion-exchange resin attrition rates.

The ion-exchange column was constructed of 4-in. glass pipe and was approximately 13 ft in over-all height. The performance tests were made with resin having particle diameters predominantly between 840 and 1100  $\mu$  when wet. The calcium feed solution concentrations

were varied between 4000 and 15,000 ppm equivalent calcium carbonate, and the regenerant solutions used for all tests were 1 wt. % sodium chloride. Data are reported for tests in which the liquid flow rates were between 40 and 75 gal/(hr)(sq ft), based on the empty-column cross section. The column was operated successfully at liquid flow rates of 100 gal/(hr)(sq ft). This liquid flow rate is very near that corresponding to fluidization of the ion-exchange resin particles. Attempts to eliminate fluidization within the column by means of the pressure drop across a cocurrent flow section at the top of the column, referred to by Jury<sup>23</sup> as the hydraulic ram, have not been completely successful to date.

These data were used to determine the number of theoretical equilibrium stages by the McCabe-Thiele method, and stage heights were computed from the actual exchange section heights. Data for three stripping runs are given in Table III-1. Typical values of the height equivalent to a theoretical stage (HETS) ranged from 0.3 to 1.0 ft. These values are approximately 10 times the corresponding values obtained by integration of the ion-exchange rate equation developed by Anderson.<sup>24</sup> This disagreement is attributed to nonuniform flow effects in the column.

Table III-1 COMPARISON OF THEORETICAL AND EXPERIMENTAL STAGES FOR A CONTINUOUS ION-EXCHANGE COLUMN\*†

No. of equilibrium stages (graphically)	Resin bed height, cm		Stage height, cm/stage		Bed effectiveness, %
	Actual	Calc.	Actual	Theoret.	
7.1	74.93	7.13	10.56	1.00	9.51
6.6	74.93	6.55	11.35	0.99	8.74
3.1	74.93	2.17	24.17	0.70	2.89

\*G. M. Drake, Jr., and F. N. Peebles, An Experimental Study of the Characteristics of a Continuous Countercurrent Ion Exchange Column, Report AECU-3463, March 1957, Table V, p. 49.

† These determinations were made on stripping sections.

Resin attrition rate measurements show 0.02 per cent fines (diameter less than 840  $\mu$ ) accumulation per pass when using a manually adjusted plug type valve to regulate the resin flow rate as compared to 2 per cent fines accumulation when using a motor-driven rotating feeder. The fines accumulation is based on the total resin inventory of the column.

These studies showed that the operation of a continuous countercurrent ion-exchange column using a moving dense bed of ion-exchange resin was satisfactory at liquid flow rates up to that corresponding to fluidization. Further work is needed for effective use of the hydraulic ram principle as a means of maintaining dense bed operations above the fluidization velocity of the resin particles.

#### Ion-exchange Studies with Polonium

Danon and Zamith<sup>25</sup> have studied the ion-exchange behavior of polonium in hydrochloric and nitric acid mediums. Adsorption by an ion-exchange resin, Dowex-1, from nitric acid solutions is unusually slow. Reducing agents that had no effect on anion exchange in hydrochloric acid solutions exerted a marked influence on these processes in nitric acid mediums. The tendency of polonium to form complexes and its oxidation reactions were discussed.

#### Fluoride Volatility Processes

The introduction of solvent-extraction processes as a replacement for the original precipitation (bismuth phosphate) separations process brought about considerable savings in fuel-processing costs. The fuel cycle is still complicated, however, and, in an effort to determine if further savings were possible, development projects on a number of alternate processes have been set up. One such project encompasses a number of nonaqueous processes that are generally referred to as fluoride volatility processes. The common feature of these processes is the conversion of uranium (or plutonium) to a volatile hexafluoride compound.<sup>26</sup> These processes offer two general advantages over the aqueous processes: (1) the product, uranium hexafluoride, is closer to the desired end product than that produced by the aqueous methods and (2) the required decontamination is more easily effected, at least potentially, by the use of two unit operations not possible in aqueous flow sheets, i.e., fractional distillation and absorption-desorption.

Processes studied to date fall into two general classes that may be characterized by the temperature range in which the initial dissolution is carried out. In the first of these, natural or slightly enriched uranium containing

little or no alloying agent is dissolved in a liquid interhalogen compound at temperatures up to 130°C. The product uranium hexafluoride is subsequently separated from the interhalogen reagent, and the volatile fission products are separated by fractional distillation. In the second class, uranium (generally enriched) alloyed with significant quantities of one or more other metals is dissolved in a fused fluoride salt bath at temperatures of 600 to 800°C. The dissolution uses hydrogen fluoride to convert the alloy metals to their fluorides and the uranium to the tetrafluoride, followed by fluorine or an interhalogen to convert the uranium to the hexafluoride. The final separation and decontamination may then be accomplished by distillation as in the low-temperature flow sheet or by absorption-desorption. Most of the work on high-temperature processes to date has been in connection with zirconium-matrix fuels.

#### Bromine Trifluoride Process

One of the low-temperature processes involves the direct fluorination of uranium metal with liquid bromine trifluoride.<sup>26,27</sup> The product of the dissolution, uranium hexafluoride, is purified and decontaminated by fractional distillation. The plutonium fluoride and fission-product fluorides are concentrated as nonvolatile residues. Subsequent recovery of plutonium can be achieved by an aqueous wash with solvent-extraction decontamination or by nonaqueous re-fluorination to form volatile plutonium hexafluoride.

1. *Continuous Dissolution of Uranium by Interhalogens.* Brookhaven National Laboratory (BNL) has been investigating the continuous dissolution of irradiated uranium in bromine trifluoride on a pilot-plant scale. Continuous dissolution promised high capacity in relatively small equipment with a very low volume of radioactive waste, and it was considered that this would enhance the economic feasibility of the process. The first experimental dissolution of uranium was accomplished in January 1957, and eight inactive dissolution runs were completed.<sup>28</sup>

The plant consisted of a dissolver (5 lb/hr of uranium) and auxiliary process equipment fabricated of monel. Special equipment components and numerous safety features were utilized. A major equipment problem was the development

of a canned-rotor pump used for circulation of the dissolver stream through an external heat exchanger. A system for continually charging slugs to the pressurized dissolver was also

at 120°C, starting with pure bromine trifluoride and progressing to solutions containing 4 mole % uranium hexafluoride. Dissolutions were carried out at rates up to that corresponding to

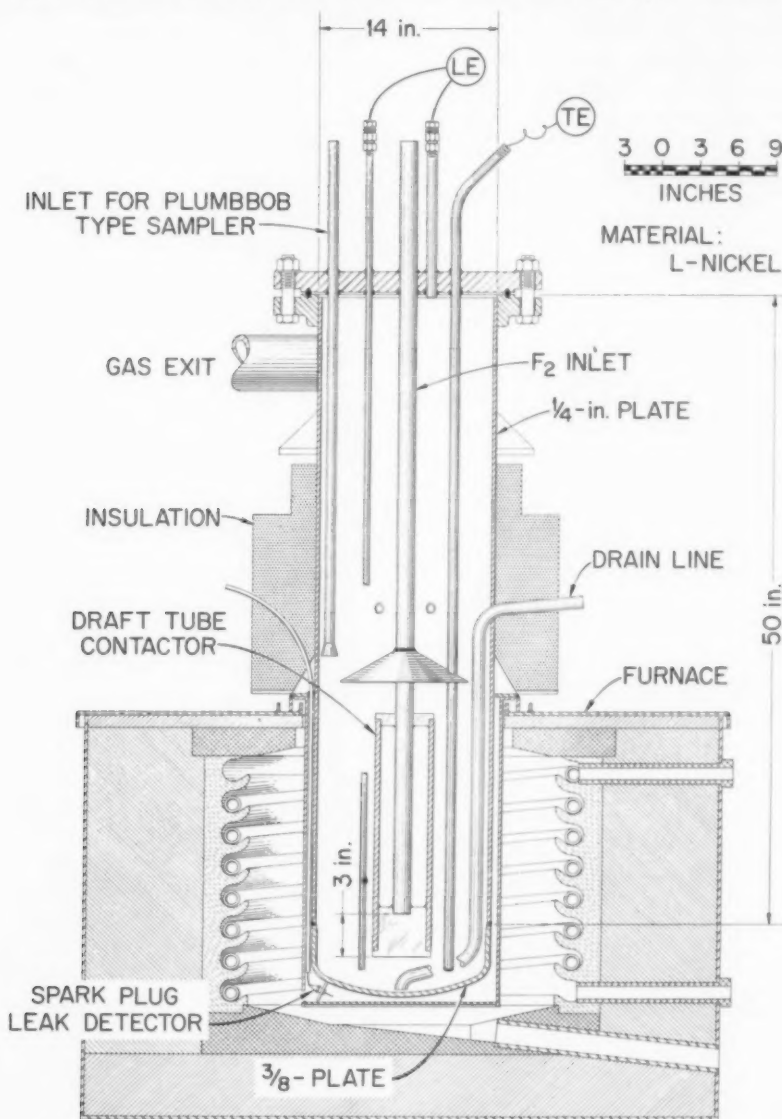


Fig. 7—Fluorinator and furnace used in a fused-salt volatility process (ORNL-CF-4-18, p. 16).

developed. Operation consisted of batch runs that were made with unirradiated slugs (1.1 in. diameter and 4 in. long) to obtain data for planning continuous runs. Eight runs were made

about 2.5 hr for 80 per cent slug dissolution. It was found that uranium hexafluoride increases the dissolution rate. Its effect in reducing slug dissolution time is marked at concentrations

up to 1 mole % becomes increasingly less in the 1 to 2 per cent range and has no effect in the 2 to 4 per cent range.

Unfortunately this plant was severely damaged, and a number of people were injured (none permanently) by an explosion on May 15, 1957. The cause of the explosion is not completely clear; it is believed to have been set off by a gas-phase reaction between uranium and interhalogens brought about by the carrying of some uranium metal out of the liquid by a slug feeder device that was used periodically to follow the dissolution rate.

#### 2. Distillation of $UF_6$ -Interhalogen Mixtures.

Uranium hexafluoride that is to be introduced into a gaseous diffusion plant must meet very high purity standards. Decontamination from fission products and from other impurities must be nearly complete. In this regard the carrier interhalogen used during dissolution must be regarded as an impurity.

To study the separation of uranium hexafluoride-bromine pentafluoride mixtures, a 70-lb batch distillation run was made in a 1.75-in.-diameter pilot-plant column<sup>29</sup> that has a 16-ft section packed with Heli-Pak 3019. During the run, a small amount of fluorine was added continuously to minimize the formation of interhalogen compounds by side reactions. During the early stages of the batch distillation, the mole fraction of bromine pentafluoride in the still pot vapor was reduced from 0.252 to 0.000247, with less than 1 per cent of the uranium hexafluoride taken overhead. This was equivalent to an HETS of about 6 in. The run was terminated when 25 per cent of the uranium hexafluoride was taken overhead. Toward the end of the run, the separation became progressively poorer, declining to essentially no separation. This was probably due to trapped bromine pentafluoride in the still pot. A material balance of 99 per cent was obtained.

#### Fused-salt Processes

Reactors fueled with enriched uranium are likely to be important for such applications as ship propulsion and as the seed core for multi-zone power reactors such as the Pressurized Water Reactor (PWR). These fuel elements are alloyed or clad with zirconium or stainless steel. They do not dissolve in liquid interhalogen compounds nor in nitric acid. A fused-

salt volatility process<sup>26,30</sup> may be applied to the processing of such fuels.

The chief steps of a fused-salt process are (1) dissolution of the alloy in molten  $NaF-ZrF_4$  with a hydrogen fluoride vapor sparge at about 600°C and atmospheric pressure, (2) fluorination of the uranium tetrafluoride to uranium hexafluoride, this product being volatilized from the melt at 1 atm and 600°C with partial decontamination, and (3) final decontamination of uranium hexafluoride by fractional distillation or adsorption-desorption.

Pilot-plant equipment for testing processes of this type is available at Argonne and Oak Ridge. The equipment at Oak Ridge National Laboratory (ORNL) consists of a hydrofluorinator, a fluorinator, and sodium fluoride absorbers to decontaminate and purify the uranium hexafluoride vapor.<sup>31</sup> The fluorinator is fabricated from low-carbon nickel (0.02 per cent carbon max.) and is 14 in. O.D., 54 in. high, and has a 1/4-in. wall. Salt capacity is approximately 1.4 cu ft. A drawing of the fluorinator is shown in Fig. 7. This equipment has only recently been placed into operation.

At ANL three preliminary runs have been made in a Mark I dissolver-fluorinator in which uranium has been volatilized from fused salt.<sup>29</sup> This unit was made of nickel and was 8 in. in diameter and 7 ft long. The sparge gas distributor was a bottom plate containing five 3/16-in. holes. In one run the uranium was put into the salt by a dissolution of uranium-zirconium alloy; in two others the uranium was added to the salt as the tetrafluoride. Bromine pentafluoride was used as the sparge gas in two runs, and fluorine was used in the third. The operating temperature was 600°C, and the pressure was approximately atmospheric. About 200 lb of salt charge was used. Melt samples were taken initially and during the sparge period by means of a spoon type sampler lowered through a gate valve in the top of the dissolver.

The results of the runs are plotted in Fig. 8 as weight per cent of uranium remaining in the salt vs sparge time. The sparge rates are shown in terms of the theoretical amount required to convert the original uranium tetrafluoride charge to uranium hexafluoride. A horizontal dashed base line is drawn showing the average of six salt blank determinations.



Stoichiometric amounts are determined by



The rate of removal of uranium increases with increasing sparge rate, and the percentage uranium removed is of the same order for equal molar ratios of sparge gas to uranium tetrafluoride charged. No difference between the sparge efficiency of fluorine and bromine pentafluoride is apparent in these tests; the uranium concentration was reduced by a factor of about 25 in 2 hr.

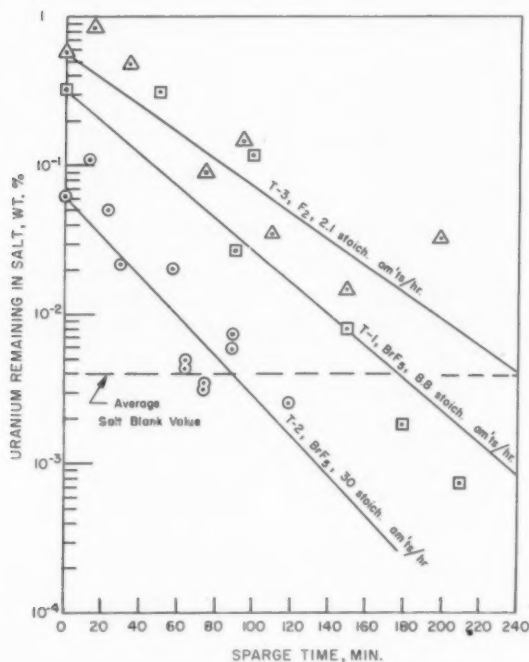


Fig. 8—Uranium removal from fused salt in pilot-plant fluorinations (Summary Report, Chemical Engineering Division, July, August, September, 1957, ANL-5789, Confidential). Run T-3,  $\text{F}_2$  sparge. Run T-1,  $\text{BrF}_3$  sparge. Run T-2,  $\text{BrF}_3$  sparge.

The Mark I dissolver has been removed and sectioned for corrosion study after 120 hr operation. A new dissolver, Mark II, has been installed for further process tests. Also a graphite cold-wall dissolver is being built by Horizons, Inc., for pilot-plant studies at Argonne.

## Process Chemistry of Fluoride Systems

A considerable amount of study has been made of the basic chemistry of the various fluoride systems of interest.

Studies of the dissolution rate of zirconium in sodium fluoride-zirconium fluoride melts indicate that the dissolution rate is not affected appreciably by the degree of impingement of the hydrogen fluoride sparge gas upon the zirconium sample. It was observed that a limited amount of dissolution occurs in the absence of hydrogen fluoride. Dilution of the hydrogen fluoride with helium does not affect the dissolution rate.<sup>32</sup> A black scale that forms on the surface of the Zircaloy during the dissolution reaction was investigated and was found to contain approximately equal weights of alpha-zirconium and fused salt.<sup>33</sup>

The dissociation pressure of sodium bifluoride ( $\text{NaHF}_2$ ) was measured from 157 to 269°C, and the free-energy and enthalpy changes for the reaction were determined.<sup>33</sup> The kinetics of the vapor-phase reaction of fluorine with iodine pentafluoride to form iodine heptafluoride has been studied from 55 to 95°C. The rate of the reaction was found to be second order with an activation energy of 14 kcal/mole.<sup>34</sup>

## Pyrometallurgical Processing

Also within the category of nonaqueous processes are the so-called "pyrometallurgical" or high-temperature processes. Ideally, these are processes in which the fuel is retained in the metallic state throughout, but also included in the definition are processes in which the metallic state may be lost momentarily, such as in passage through a molten-salt bath, and processes in which the metal may be converted to a salt in one step and back to the metal in a succeeding step. All are characterized by the necessity of high temperatures, from several hundred degrees centigrade to well above the melting point of uranium.

An excellent review of the principles of various pyrometallurgical operations was presented at the Belgium Symposium on the Reprocessing of Irradiated Fuels.<sup>35</sup> An outline (see Table III-2) was presented as being suitable for a systematic examination of this field, and to

this outline have been added some illustrative examples.

Table III-2 OUTLINE OF PYROMETALLURGICAL OPERATIONS

Non-Chemical Separations

- Fractional distillation or sublimation
  - Distillation of Pu or fission products from U
  - Separation of Po from Bi
- Fractional crystallization
  - Without added solvent
    - Zone melting
  - With added solvent
    - Fractional crystallization of U and fission products from metal solutions (e.g., Zn or Hg)
- Liquid-liquid partition
  - Extraction of Pu from a molten U phase with molten Mg or Ag
- Liquid-solid extraction
  - Extraction of Pu from finely divided U with molten Mg

Separations by Selective Oxidation

- Oxides and Carbides } Drossing of fission products through formation of oxides or carbides
- Nitrides and sulfides
- No present example
- Halides
  - Selective removal of fission products and/or Pu by contacting liquid-metal phase with molten halide salt mixtures (e.g., LMFR\* fuel process)

Separations by Cyclic Oxidation-Reduction

Chemical

- Van Arkel-DeBoer method of thermal decomposition of metal iodides and Gibson reaction for formation of U or Pu halide and subsequent reduction of halide to metal

Electrochemical

- Use of electrochemical cell for refining irradiated Th

\* Liquid Metal Fuel Reactor.

Several power reactor systems (see Table III-3) are now under construction or are planned in which it is intended to process the fuel by pyrometallurgical methods. These pyrometallurgical processing facilities were described at the Belgium conference.<sup>36</sup> They are pilot-plant facilities that will provide engineering experience and information on the economics of these processes. Potential savings by pyrometallurgical methods are thought to be possible through:

1. Reduction of fuel inventory through ability to process short-cooled material.
2. Elimination of chemical conversion.
3. Ability to utilize low but adequate fission-product decontamination in conjunction with remote fuel fabrication.
4. Recovery of expensive alloying agents.

5. Direct production of dry, concentrated fission-product wastes.

6. Avoidance of many expensive critical mass problems.

7. Operation of a small, compact processing plant at reactor site to avoid shipping costs.

Table III-3 REACTOR SYSTEMS EMPLOYING PYROMETALLURGICAL FUEL-PROCESSING METHODS

Reactor	Type	Fuel
EBR-II	Fast breeder, sodium cooled	Pu or enriched U alloys
SRE*	Thermal, graphite moderated, sodium cooled	Slightly enriched U
LMFR	Thermal, graphite moderated, heat removed in circulating fuel	Dilute solution (800 ppm) of U <sup>235</sup> or U <sup>238</sup> in Bi

\* Sodium Reactor Experiment.

### EBR-II Melt Refining Process

The first plant operation of a pyrometallurgical process<sup>36</sup> will be that now being designed for the Experimental Breeder Reactor (EBR-II)

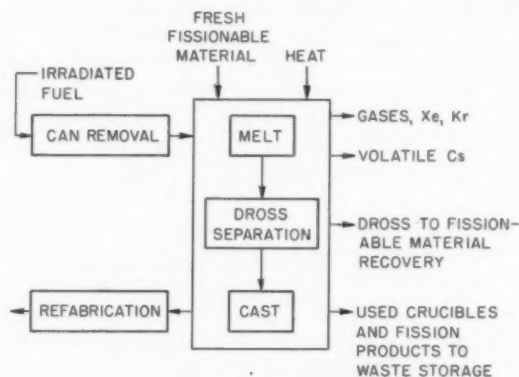


Fig. 9 -- Melt refining process.

fast breeder reactor. The core processing method will be oxide drossing, or perhaps a more descriptive term is melt refining. It involves melting the fuel in an oxide crucible, either zirconia or magnesia, and holding it molten at ~1300°C for several hours. During this period, volatile fission products are evolved from the melt, and fission products more reactive than uranium are removed in a reaction layer that

forms along the crucible walls. The noble fission products are not removed. A flow sheet for this process is presented in Fig. 9. An example of a remotely operated melt refining furnace is shown in Fig. 10.

are precision cast by a procedure known as injection casting.<sup>36</sup> The procedure consists in lowering a cluster of evacuated Vycor tubes into the melt and at the same time pressurizing the furnace to drive the metal into the Vycor

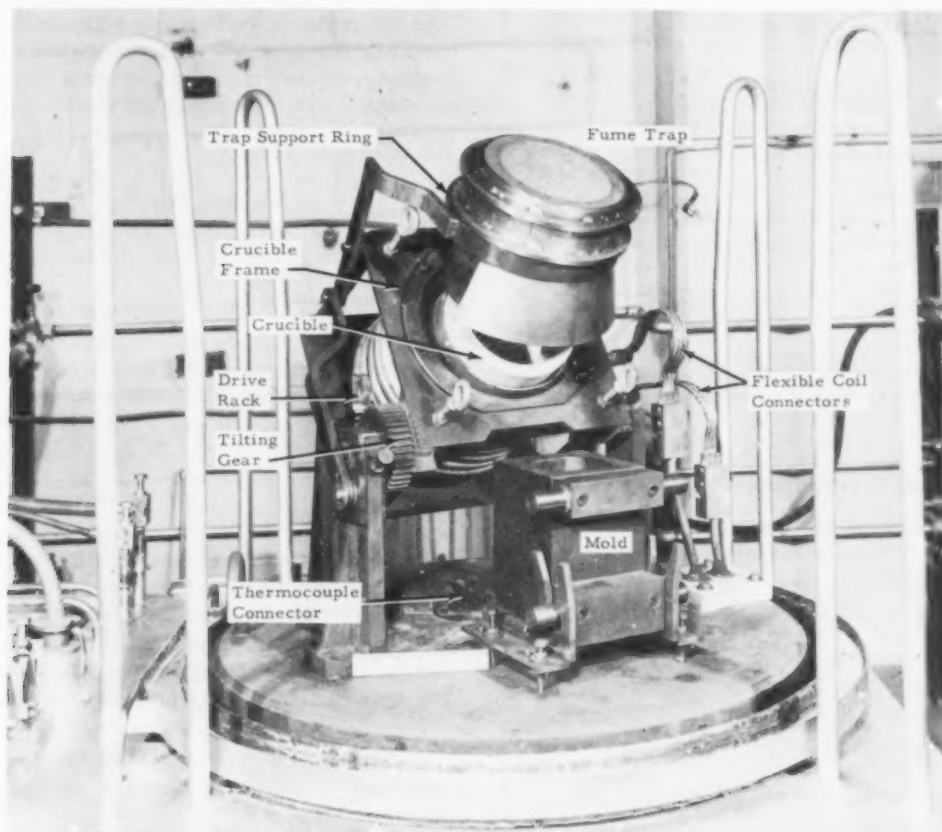


Fig. 10—View of melt refining furnace.

Since the noble fission products are not removed, they build up under continued fuel recycle, eventually reaching equilibrium concentrations that are dependent on the percentage of new fuel added per cycle. Table III-4 gives the equilibrium concentration for the addition of 5 wt. % new metal per pass. These alloying elements have been found to be beneficial, increasing markedly the irradiation stability of the fuel elements. With the alloying agents present, 2 per cent burn-up of the total atoms is a realistic goal.

After fuel purification the pin type fuel elements (0.144 in. in diameter by 14.22 in. long)

molds. Tolerances of 0.001 in. diameter have been produced in 96 per cent of the castings.

At North American Aviation a somewhat similar program is under way to develop equipment for the pyroprocessing of fuel from the Sodium Reactor Experiment (SRE).<sup>36</sup>

#### Processing of U-Bi Reactor Fuels by Fused-salt Extraction

The Liquid Metal Fuel Reactor (LMFR) under development at Brookhaven uses a fuel that is a solution of uranium, magnesium, and zirconium in bismuth.<sup>36</sup> The process consists in

contacting the liquid bismuth fuel with a molten chloride salt mixture to remove those fission-product chlorides more stable than uranium chloride. Gaseous fission products are removed by reducing the pressure or by gas sparging. This process has been well documented in the open literature within recent years.

Table III-4 CALCULATED EQUILIBRIUM FISSION-PRODUCT CONCENTRATION  
(5 Wt. % New Metal Per Cycle)

Element	Equilibrium concentration, wt. %
Zirconium	0.10
Niobium	0.01
Molybdenum	3.42
Technetium	0.99
Ruthenium	2.63
Rhodium	0.47
Palladium	0.30

### Fractional Crystallization Processes

Two processes are currently under investigation which involve dissolution of uranium in a metal solvent. These are the Hermex process<sup>37,38</sup> under development at ORNL which employs mercury as a uranium solvent and another process under development at ANL which uses zinc as a uranium solvent.<sup>39</sup> In both processes purification mechanisms of gaseous fission-product evolution and oxide drossing of reactive fission products are operative, but in addition to these is the fission-product-uranium separation that results on precipitation from solution of a uranium-solvent metal intermetallic compound. This product is separated from the bulk of the solution, and the uranium is subsequently recovered by decomposition of the intermetallic compound and vaporization of the solvent metal. The uranium is then consolidated by melting. By use of different metal solvents the process engineer can vary the solubility relations, the nature of the phases formed, and the operating temperatures to obtain the desired separations.

1. *Hermex Process.* Dissolution rates of uranium in boiling mercury and in boiling amalgams with sodium, magnesium, and bismuth were measured. The dissolution rates were increased by magnesium (0.1 to 0.5 wt. % concentrations) but were decreased by bismuth and

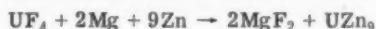
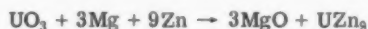
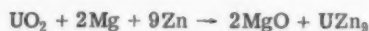
sodium. The solubility of uranium was also markedly increased by the presence of magnesium. Dissolution rates in mercury, 7 mg/(cm<sup>2</sup>)(min), and in magnesium-mercury amalgams, 7 to 19 mg/(cm<sup>2</sup>)(min), were concluded to be satisfactory for process considerations.

In preliminary work in glass apparatus, decontamination from the highly active and volatile fission products was good, whereas that from the noble metals was relatively poor.

2. *Zinc Process.* The use of zinc was first reported by Knighton<sup>39</sup> at the June meeting of the American Nuclear Society. The uranium compound that precipitates from zinc is UZn<sub>3</sub>, which has the desirable characteristics of being nonpyrophoric and of being easily formed in large crystals so that separation of the zinc mother liquor may be accomplished by filtration through porous mediums (porous graphite alundum). Solubility data for uranium and various fission-product solutes were also presented by Knighton.

Recovery of uranium from UZn<sub>3</sub> has been demonstrated on a small scale (150 g). The zinc was retorted at 950°C, and the uranium was coalesced by heating to 1200°C. A product containing only 30 ppm of zinc was produced.

In connection with this development work, it was found possible to reduce various uranium compounds with magnesium in a zinc solvent. The following chemical reductions were effected.



A literature survey has been made by Nathans<sup>40</sup> of metal solubilities in zinc.

### Pyrometallurgical Process Development

#### for Th-U Fuel

A number of investigations on the processing of thorium-uranium fuels by pyrometallurgical methods are under way.<sup>41-43</sup> Processes that seem to warrant further investigation are the van Arkel-DeBoer iodide process, molten-salt slagging, and fission-product vaporization from hydrided and dehydrided thorium just below the melting point. Removal of fission products in oxide, carbide, nitride, or sulfide drosses, or

by arc zone melting, while offering some decontamination, do not appear to warrant further investigation.

1. *Fission-product Vaporization by Arc Melting.* In Table III-5 are presented decontamination results of small-scale studies on vaporization of fission products by arc melting.<sup>44</sup> The results follow predictions based on vapor-pressure data. Strontium and cesium are effectively removed; cerium and rare earths are partially removed; the refractory metals such as zirconium and ruthenium are not removed. Tellurium shows variable behavior. Protactinium removal, which is not desirable, is increased by higher temperatures and longer heating times. It is suggested that consumable electrode arc melting would be a practical engineering procedure.

Table III-5 FISSION-PRODUCT REMOVAL FROM IRRADIATED Th-3 WT. % U ALLOY BY ARC MELTING

Temp., °C	Time, min	Weight, g	Fission-product removal, %							
			Ce	R.E.*	Cs	Sr	Te	Zr	Pa	Ru
1650	32	2.85	25	52	99	100	20	0	1	
1800	42	4.10	35	65	99	100	73	0	1	
1850	24	2.57	85	78	95	99	89	0	31	0
1850	20	2.61			99	99	96	0	25	0
1860	16	2.32	66	89	80	92	55	0	0	
1800	16	2.43	74	87	88	93	52	0	0	
1850	16	2.68	80	94	82	94	45	12	0	

\* Rare earths.

2. *Fission-product Removal by Molten-salt Slagging.* On a small scale (10 g), thorium-10 wt. % uranium alloys have been partially decontaminated by induction melting the metal on a compacted bed of calcium fluoride. The molten metal slowly works its way through the salt bed, melting the salt in the immediate vicinity. The reactive and volatile fission products are partially removed, whereas the noble metals and protactinium are not appreciably extracted.<sup>41,45</sup> Data from this run are presented in Table III-6.

### Electrorefining Process for Fuel Purification

A status and review report<sup>46</sup> has been issued on the electrorefining process, work on which has been terminated at KAPL because of basic changes in the Laboratory program. The process consists in making the contaminated fuel the anode in a high-temperature electrolysis

cell employing a fused-salt, electrolyte. On passage of a current the fuel dissolves anodically and is deposited at the cathode. If desired, the cathode may be a metal such as manganese which forms a low-melting alloy with uranium. Then, as uranium is deposited, the alloy is formed, drips off, and may be collected or continuously removed. Later the alloying metal may be distilled away.

Elements more noble than uranium settle as an insoluble sludge at the anode. Those more electropositive remain in the salt bath. Fission-product removals (both noble and electro-

Table III-6 DECONTAMINATION DATA FOR SALT-BED PROCESSING OF IRRADIATED Th-10 WT. % U ALLOY (CaF<sub>2</sub> BED)

Bed depth, in.	Fission-product removal, %								Fuel loss, %	
	R.E.	Ce	Cs	Te	Sr	Ru	Pa	Zr	Th	U
1.0	37	35	35	69	59	0	7	8	1.4	
1.5	73	75	45	82	70	0	7	7	2.4	3
2.7	75	84	39		62	0	6	2	4.3	0
4.5	95	96	78		95	8	6	3	8.6	1
6.1	97	98	92		97	0	4	0	11.6	3

positive) were generally in excess of 90 per cent and often in excess of 99 per cent. These removals were demonstrated for both lightly irradiated (tracer activity) uranium and for synthetic alloys containing various fission products in 1 wt. % concentrations. It was demonstrated that decontamination from both the noble and active metals was satisfactory, even after as many as 15 bath throughputs. However, sharp separation of plutonium from uranium was not possible with the particular salt baths employed. It was indicated therefore that the process would have its greatest potential in the processing of relatively pure fissile fuels.

Various modes of operation and equipment designs are discussed. Methods are described for calculating fission-product decontamination obtainable by electrorefining. A detailed economic evaluation was not made, although certain economic factors were discussed.

### Blanket Processing Methods

1. *Magnesium Extraction of Plutonium from a Molten-uranium Phase.* Molten magnesium, which is immiscible with molten uranium, may be used to extract plutonium from uranium. Plutonium distributes between molten uranium



and magnesium with a distribution coefficient of about 2 (wt. % basis). The plutonium may be separated from the magnesium by volatilization of the latter.

A study of the separation of plutonium and uranium by molten magnesium was carried out by Feder et al.<sup>47</sup> Distribution coefficients were measured for plutonium concentrations up to 1 wt. %, and, by use of uranium alloying agents, over a temperature range of 930 to 1200°C. Plutonium transfer was found to be very slow unless the phases were agitated. No effect of plutonium concentration up to 1 wt. % concentration on the distribution coefficient was found. Distribution coefficients were higher at the lower temperature.

Work was also reported on the transfer of plutonium from finely divided solid uranium (hydride and dehydrided) to molten magnesium. By hydriding and dehydriding, as much as 80 per cent of the plutonium was made available for solution in magnesium at 800°C. Additional work is required to ascertain the method of extracting the remainder.

Development of multikilogram scale equipment for the extraction and distillation operations has been reported.<sup>48</sup> Testing of various container materials indicates the most promising to be graphite, tantalum, and refractories such as alumina or magnesia.

### Fundamental Chemistry

1. *Ceramic Oxide-Uranium Interactions.* A study of the interaction of uranium and its alloys with ceramic oxides has been carried out.<sup>49</sup> The studies include (1) wettability of ceramics, (2) products of reaction, (3) mechanism of reaction, (4) contamination of molten uranium by crucible material, and (5) effect of alloying additions on these.

Measurements are reported by Feder and Rosen<sup>49</sup> of contact angles of drops of uranium and its alloys on ceramic plaques. From these measurements were calculated densities and surface tensions.

2. *Plutonium and Fission-product Distribution Between Molten Uranium and Halide Mixtures.* The distribution of plutonium between molten uranium and mixtures<sup>50</sup> of uranium trifluoride with barium chloride or fluoride has been measured at temperatures of 1200 to 1400°C. The equilibrium constant for the re-

action  $\text{Pu} + \text{UF}_3 = \text{PuF}_3 + \text{U}$  was found to be  $72 \pm 50$  mole %. This corresponds to a standard free-energy change for the reaction at 1200°C of approximately -13 kcal, which agrees well with the estimated value.

On the 20-g uranium scale at least a 60-min contact between phases is required to establish equilibrium. Fission-product removals from the metal are greater than 99 per cent under a variety of conditions, but, owing to the complications of self-slagging effects, the results cannot be interpreted in terms of equilibrium constants. About 80 per cent of fission products cesium and about 20 per cent of the strontium volatilizes under these conditions.

The same final equilibrium is achieved if the salt mixtures are initially made up with uranium tetrafluoride instead of the trifluoride, reduction by the metallic phase being substantially complete.

### Calculated Fission-product Spectra

#### in Discharged Fuel from Fast Reactors

Calculations of fission-product spectra, total curies, and energy-dissipation rates are presented for fast-fissioned reactor fuels subjected to a wide range of operating conditions in an article by Dillon and Burris.<sup>51</sup> These calculations are similar to previous ones made by Blomeke<sup>52</sup> for thermal-fissioned uranium fuels.

### Corrosion

Corrosion is a subject that is an integral part of each process-development program. Because it is a problem that lends itself to setting up specific programs, however, much of the literature is reported under this specific heading. In this section an attempt will be made to cover progress on programs that have been set up to cover specific corrosion problems in a systematic way.

### Solvent-extraction Processes

New head-end treatments for existing solvent-extraction plants are being developed to handle stainless-steel and zirconium-matrix fuels. They generally involve nitric acid-chloride mixtures (see pp. 4-6). In continuing tests that are being made at Battelle Memorial

Institute (BMI),<sup>53</sup> Haynes-21, tantalum, titanium, and zirconium appear promising in boiling dissolver solutions (2M HCl-5M HNO<sub>3</sub>). All have rates less than 1.5 mils/month. Cobalt-base alloy S-816 corroded at a maximum of 3.2 mils/month. Measured potentials of titanium- and tantalum-uranium couples in the same environment indicate that hydrogen evolution is likely to occur in tantalum. As hydride formation in both tantalum and titanium is detrimental, impressed voltage tests are being made for extended periods to determine the extent, if any, of metal degradation.

Hanford and Idaho are also conducting tests on hydrochloric acid-nitric acid mixtures. The former is determining the minimum amount of nitric acid required in hydrochloric acid to yield reasonable corrosion rates on titanium.<sup>54</sup> Idaho<sup>55</sup> has found that the presence of dissolving alloy reduces corrosion of titanium by a factor of 100 in these solutions when the Cl<sup>-</sup> to NO<sub>3</sub><sup>-</sup> ratio is less than 4.

Materials<sup>53,56</sup> that appear promising for the Zircex process dissolver (dissolution of UCl<sub>3</sub> in HNO<sub>3</sub>) are cobalt-base alloys S-816 and Haynes-21.

Tests indicated very low rates of attack on titanium in boiling aluminum nitrate waste; the limitation is in the higher rates<sup>55</sup> of corrosion during decontamination procedures, 15 to 20 mils/month.

### Fused-salt Volatility Process

Containment of the fused-fluoride dissolution process for zirconium-matrix fuels continues to be a problem of some magnitude. The most promising materials are nickel alloys and graphite.

ANL is concerning itself primarily with graphite, whereas ORNL (through BMI) is studying metals.<sup>53,57</sup> Of the metals, nickel-molybdenum alloys appear the most promising. Graphite is chemically compatible; recent tests of 1000 hr duration show dimensional change rates of less than 0.1 mil/day. Factors involved in the use of graphite include its lack of strength and ductility and porosity (diffusion of uranium and fission products).

### Pyrometallurgical Processes

Corrosion problems associated with pyrometallurgical processes that are being investigated

include materials for contact with molten uranium and its alloys and magnesium. A recent report<sup>58</sup> describes an approach to the study of molten-uranium reactions with graphite at temperatures ranging from 1150 to 1400°C. The identification of reaction layers resulting from varying exposures was made, and rates of dimensional change of the graphite were measured. Corrosion rates at 1200°C were about 0.3 mil/day and, at 1400°C, 1.5 mils/day.

Tantalum borides had previously been found to be reasonably satisfactory in contact with molten uranium. A series of equilibrium experiments at 1800°C resulted in the identification of tantalum monoboride as the most stable compound and the one most likely responsible for the protection of tantalum.<sup>59</sup>

A survey and testing program is under way for the containment of uranium-thorium-aluminum alloys. Tantalum, niobium, and zirconium have not proved satisfactory.<sup>60</sup>

Studies of metals in contact with molten magnesium at 950°C are being made.<sup>59</sup> Materials being investigated include stainless steel type 446, Croloy-2 1/4, mild steel, and tantalum. The latter appeared nearly unaffected in six-day tests, mild steel was badly attacked, and the other two metals were marginal.

### Fluidized Beds

Corrosion coupons from two fluidized-bed pilot-plant units were recently evaluated after 80 hr exposure.<sup>59</sup> Three stainless steels (304, 309, and 347) were penetrated a maximum of 0.06 mil in the uranium trioxide to uranium dioxide (hydrogen at 575°C) reduction column. Dimensional change of monel, Inconel, and Hastelloy B did not exceed 0.1 mil in the lower portions of the hydrofluorination unit (hydrogen fluoride at 400 to 600°C) which converts uranium dioxide to uranium tetrafluoride. In the upper portions, where moisture becomes a significant part of the vapor phase, penetration increased to 4 mils for monel and 0.2 mil for Inconel and Hastelloy B.

Corrosion information is being obtained on a pilot-plant waste calciner at Idaho. The process consists in spraying wastes containing aluminum nitrate into a fluidized bed at 400°C. Carpenter-20, stainless steel type 347, and a structural-steel coupon exposed for 436 hr showed little attack.

## Homogeneous Reactor Processing

One of the advantages of homogeneous reactors is that a side stream of fuel can be continuously or periodically withdrawn and processed to reduce the fission-product poisons to some stable and predetermined level. The efficiency of processes developed for this purpose need not be high.

A fused-chloride process for the bismuth-uranium fuel from the LMFR is being developed.<sup>61</sup> Recently a series of tests was concluded in which bismuth-uranium fuel was circulated in a loop in the Brookhaven reactor for generation of fission products.<sup>62</sup> The fuel was contacted with chloride salts in the loop at 500°C. Distribution of volatile fission products between the fuel and helium was obtained as well as partition data of nonvolatile fission products between fuel and salt. Information on corrosion products is also presented.

There is also study of a fused-chloride head-end treatment of uranium-bismuth fuels for solvent extraction.<sup>63</sup> The fuel is contacted with a solution of bismuth chloride in a potassium chloride-lithium chloride mixture to extract uranium and fission products.

Work on the chemical-processing problems connected with the aqueous homogeneous reactor have been reported.<sup>64</sup> The Homogeneous Reactor Test chemical-processing plant has been installed in conjunction with the reactor and tested with natural uranium solution for a total of 1200 hr operation.

Laboratory studies have shown that a method, based on  $\text{UO}_4$  precipitation, for decontaminating the uranium in the hydroclone underflow pot will make possible rapid return of the uranium to the reactor circuit. The process consists in separating soluble uranyl sulfate from insoluble fission and corrosion products at a temperature below 100°C and precipitating  $\text{UO}_4$  from the clarified solution. The  $\text{UO}_4$  is washed free of such soluble poisons as cesium and nickel and is dissolved in a stoichiometric amount of  $\text{D}_2\text{SO}_4$  by heating to destroy the peroxide. This solution may then be returned to the reactor. Uranium losses for the process are 0.2 per cent; decontamination from cesium and nickel is adequate.

## References

1. Reactor Technology and Chemical Processing, Volume IX, Proceedings of the International Conference in Geneva, 1956. (Available from International Documents Service, Columbia University Press, 2960 Broadway, New York 27, N. Y.)
2. Symposium on the Reprocessing of Irradiated Fuels at Brussels, Belgium, May 20-25, TID-7534. (Unclassified AEC report.)
3. R. G. Geier, in TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, p. 107. (Unclassified AEC report.)
4. H. W. Alter, R. Fowler, and J. L. Mewherter, A One-cycle Process for the Recovery and Decontamination of Plutonium, KAPL-1748, January 1957. (Unclassified AEC report.)
5. J. K. Davidson and W. O. Haas, KAPL-1543, July 1956. (Confidential AEC report.)
6. B. F. Judson, Performance of a Plutonium Reflux Solvent Extraction System, HW-49441A, March 1957. (Unclassified AEC report.)
7. R. B. Richards, Chemical Processing Department, Research and Engineering Operation, Monthly Report for May 1957, HW-50089J. (Secret AEC report.)
8. J. H. Flanary, J. H. Goode, R. G. Mansfield, and R. P. Wischow, ORNL-2235, April 1957. (Confidential AEC report.)
9. J. H. Goode, *Nucleonics*, 15: 68-71 (February 1957).
10. Report of the Chemistry and Chemical Engineering Section for August, September, October 1956, KAPL-1620. (Confidential AEC report.)
11. Report of the Chemistry and Chemical Engineering Section for November and December 1956, and January 1957, KAPL-1696. (Confidential AEC report.)
12. James D. Moore, *Journal of Metals*, 9: 757-761 (June 1957).
13. Dixon Callihan, *Nucleonics*, 14(7): 38-41 (1956).
14. Norman Ketzlack, *Chemical Engineering Progress*, 53(7): 357 (1957).
15. Sharpie et al., "Progress in Nuclear Energy," Vol. 1, Chap. 8, McGraw-Hill Book Company, Inc., New York, 1956.
16. P. A. Haas, E. O. Nurmi, M. E. Whatley, and J. R. Engel, *Chemical Engineering Progress*, 53(4): 203 (1957).
17. James C. Bresee, Design and Performance of a Dual-clone Liquid Separator, CF-56-3-171, Mar. 26, 1956. (Unclassified AEC report.)
18. J. L. Straughn and W. B. Tarpley, Investigations to Determine the Feasibility of Ultrasonic Liquid-Liquid Extraction, NYO-7936, February 1957. (Unclassified AEC report.)
19. N. K. Hiester and R. C. Phillips, *Chemical Engineering*, 61: 161-180 (October 1954).



20. F. R. Bruce, in TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, pp. 303-331, May 1957. (Unclassified AEC report.)
21. D. E. Armstrong et al., *American Institute of Chemical Engineers*, 3: 3286 (1957).
22. G. M. Drake, Jr. and F. N. Peebles, An Experimental Study of the Performance Characteristics of a Continuous Countercurrent Ion Exchange Column, AECU-3463, March 1957. (Unclassified AEC report.)
23. S. H. Jury, A Continuous Countercurrent Ion Exchange Column with High Production Capacity Due to Freedom from Fluidization, CF-53-1-213, 1953. (Unclassified AEC report.)
24. N. T. Anderson, A Study of the Reaction Rate for the Ion Exchange System Dowex-50 Resin, Calcium, and Sodium under Flow Conditions, University of Tennessee Thesis (MS), 1956.
25. J. Danon and A. A. L. Zamith, *Journal of Physical Chemistry*, 61: 431 (1957).
26. S. Lawroski, in TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, pp. 479-497. (Unclassified AEC report.)
27. R. C. Vogel and R. K. Steunenberg, TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, pp. 498-559. (Unclassified AEC report.)
28. G. Strickland, F. L. Horn, and R. Johnson, Pilot Plant Fluorination of Uranium Fuel Elements by Bromine Trifluoride, BNL-457 (I-21), July 26, 1957. (Unclassified AEC report.)
29. Summary Report, Chemical Engineering Division, July, August, September 1957, ANL-5789. (Confidential AEC report.)
30. G. Cathers, TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, pp. 560-573. (Unclassified AEC report.)
31. R. P. Milford, CF-57-4-18, April 1957.
32. Summary Report, Chemical Engineering Division, January, February, March 1957, ANL-5730. (Confidential AEC report.)
33. Summary Report, Chemical Engineering Division, April, May, June 1957, ANL-5759. (Confidential AEC report.)
34. J. Fischer and R. K. Steunenberg, *Journal of American Chemical Society*, 79: 1876-1878 (April 20, 1957).
35. H. M. Feder, TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, pp. 667-718. (Unclassified AEC report.)
36. J. H. Schraidt, W. A. Rodger, M. Levenson, S. Lawroski, D. C. Hampson, J. Graae, L. F. Coleman, L. Burris, G. J. Bernstein, and G. A. Bennet, TID-7534, Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, pp. 748-804. (Unclassified AEC report.)
37. B. H. Morrison and R. E. Blanco, The Hermex Process for Metal Decontamination by Mercury Processing, CF-56-1-151, January 1956. (Unclassified AEC report.)
38. O. C. Dean, E. Sturck, B. H. Morrison, and R. E. Blanco, Status of the Hermex Process, ORNL-2242, August 1957. (Unclassified AEC report.)
39. J. B. Knighton, H. M. Feder, L. Burris, and A. A. Chlenskias, Use of Zinc in Pyrometallurgical Processing of Nuclear Fuels, Presented at American Nuclear Society Meeting, June 1957 (unpublished).
40. M. W. Nathans, A Survey of Metal Solubilities in Liquid Zinc, ANL-5753, July 1957. (Unclassified AEC report.)
41. S. G. Buyers, Pyrometallurgical Processing for Thorium-Uranium Fuel, NAA-SR-1724, October 1956. (Unclassified AEC report.)
42. N. D. Potter, Solid and Liquid Drossing of Thorium Containing Tracer Level Fission Products, NAA-SR-1734, April 1957. (Unclassified AEC report.)
43. R. D. Burch and C. T. Young, Fission Product Separation from Thorium-Uranium Alloy by Arc-zone Melting, NAA-SR-1735, April 1957. (Unclassified AEC report.)
44. E. W. Nurback and A. G. Buyers, Decontamination of Thorium-Uranium Alloy by Nonconsumable Electrode Arc-melting, NAA-SR-1989, September 1957. (Unclassified AEC report.)
45. A. G. Buyers, J. Chillon, and W. E. McKee, Removal of Fission Products from Molten Thorium-Uranium Alloy Resulting from Gravity Flow Through Frozen Calcium Fluoride Beds, NAA-SR-2047, October 1957. (Unclassified AEC report.)
46. L. W. Niedrach, A. C. Glamm, and G. R. Fountain, The Behavior of Representative Fission Products and Plutonium in the KAPL Electrorefining Process and a Review of the Status of the Process, KAPL-1692, March 1957. (Unclassified AEC report.)
47. H. M. Feder, E. Greenberg, M. W. Nathans, and R. L. Nuttall, Separation of Plutonium and Uranium by Liquid Magnesium, Paper presented at American Chemical Society Meeting, April 7-12, 1957 (unpublished).
48. I. O. Winsch and L. Burris, *Chemical Engineering Progress*, 53: 237 (May 1957).
49. H. M. Feder, N. R. Chellew, and C. L. Rosen, Introduction of Uranium and Its Alloys with Ceramic Oxides, ANL-5765, July 1957. (Unclassified AEC report.)
50. F. S. Marten and E. W. Hooper, *Journal of Inorganic and Nuclear Chemistry*, 4: 93-99 (1957).
51. I. G. Dillon and L. Burris, *Nuclear Science and Engineering*, 2: 567-581 (1957).
52. J. O. Blomeke, Nuclear Properties of  $U^{235}$  Fission Products, ORNL-1783, 1955. (Unclassified AEC report.)

53. Chemical Technology Division Monthly Report, May 1957, ORNL-2361, pp. 39-42. (Confidential AEC report.)
54. Chemical Research and Development Monthly Report, August 1957, HW-52303C, p. 15. (Secret AEC report.)
55. Technical Progress Report for January through March 1957, IDO-14410, p. 32. (Confidential AEC report.)
56. Monthly Program Summary, September 1957, CF-57-9-101, p. 5. (Confidential AEC report.)
57. Chemical Engineering Division Summary Report, April through June 1957, ANL-5759. (Confidential AEC report.)
58. E. L. Swarts, The Action of Molten Uranium on Graphite, KAPL-1765, Apr. 9, 1957. (Unclassified AEC report.)
59. Chemical Engineering Division Summary Report, January through March 1957, ANL-5730, p. 93. (Confidential AEC report.)
60. Semi-Annual Summary Research Report (Chemistry), ISC-834, p. 17, July through December 1956. (Unclassified AEC report.)
61. O. E. Dwyer, *American Institute of Chemical Engineers*, 2: 163-168 (1956).
62. C. J. Raseman, H. Susskind, and C. H. Waide, *Chemical Engineering Progress*, 53: 68F-92F (February 1957).
63. Monthly Program Summary, Chemical Technology Division, September 1957, CF-57-9-101. (Confidential AEC report.)
64. Chemical Technology Division Annual Progress Report For Period Ending August 31, 1957, ORNL-2392. (Confidential AEC report.)

## WASTE DISPOSAL

During the past few months two comprehensive documents have become available on the subject of waste handling. One session of the Brussels meeting (see Appendix for a list of the papers)<sup>1</sup> was devoted to the subject. Also a survey of the problem has been prepared for the National Academy of Science by Oak Ridge.<sup>2</sup>

### Complete Waste-disposal Systems

The radioactive-waste-disposal system planned for use at Shippingport for the PWR has been reported by LaPointe.<sup>3</sup> Waste discharged to the

capacity is provided to store radioactive gases for the maximum expected duration of a weather inversion, which is five days.

The waste-disposal system uses (1) natural decay, (2) concentration and storage, and (3) dilution. There is a central waste-processing area where the wastes are segregated, processed or stored, and ultimately disposed of as outlined.

Radioactive liquid processing is indicated schematically in Fig. 11. The system makes use of ion-exchange demineralizers and vapor compression evaporation. Concentrates are solidified with concrete and shipped out for ocean

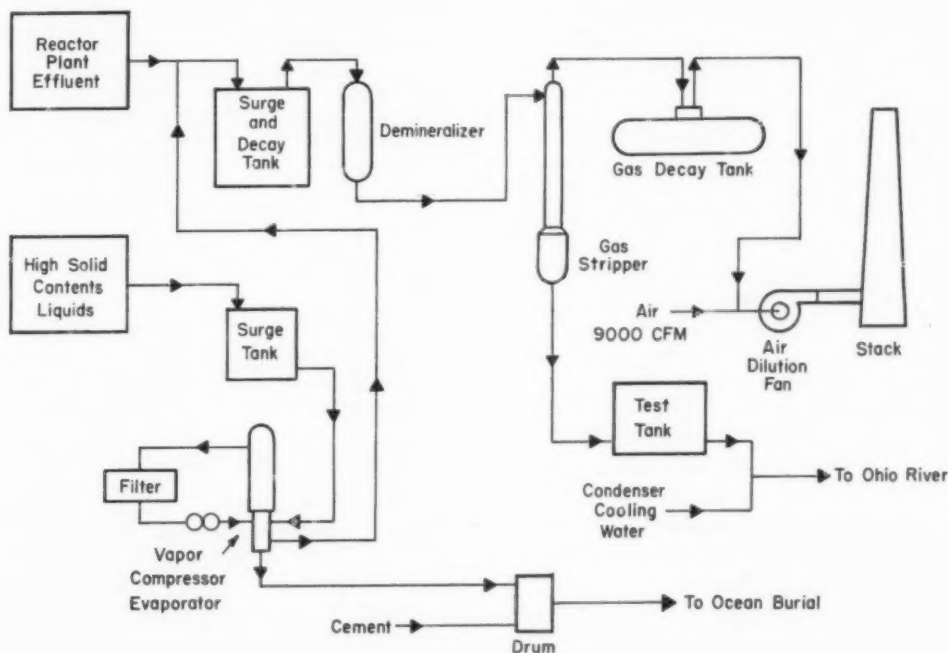


Fig. 11—Flow diagram of radioactive liquid and gaseous waste-disposal system.

Ohio River and to the air will not exceed 10 per cent of the maximum permissible concentration recommended in National Bureau of Standards Handbook 61. Another design criterion adopted because of the Donora incident is that sufficient

burial. Overheads are diluted and sent to the Ohio River.

The solid disposal system is indicated in Fig. 12. Combustible wastes are burned in an incinerator. Small noncombustible wastes are

put in drums and sent out for ocean burial. Resins and wastes too large to ship are stored on site. A summary of expected wastes is given in Table IV-1.

### Operating Experience

In the Purex tank farm some tanks that have been receiving fresh waste have been giving off brown fumes. Samples of brown fume evolution showed the presence of nitrogen dioxide, nitrous oxide, hydrogen, and carbon dioxide, the nitrogen dioxide being of the order of 0.1 per cent. The amounts of nitrogen dioxide found could easily be produced by radiolysis of nitrite solutions at a high pH.

Laboratory studies<sup>4</sup> of this problem have indicated:

Table IV-1 RADIOACTIVE WASTES AT PWR

Type	Monthly amount	Special activity,* $\mu\text{C}/\text{cm}^3$
Reactor plant effluent	< 16,000 gal	7.6†
High-solid-content liquids	7,500 gal	1.7†
Spent resin	36 cu ft	< 0.27
Combustible wastes, av. max.	3,000 lb	10 <sup>4</sup>
	10,000 lb	Variable

\*Total activity of liquids and gases, ~ 20 curies/day.

†Volatile.

‡Nonvolatile.

occurs if manganese dioxide or potassium permanganate is added to the waste, but nitrogen dioxide is evolved rapidly if manganous salts or hydroxide are added.

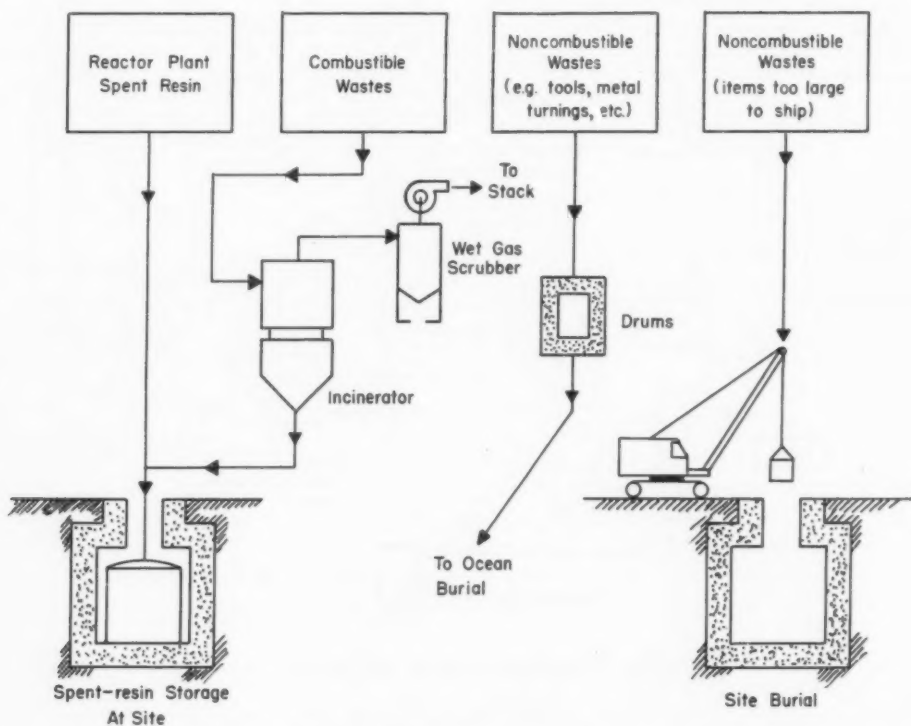


Fig. 12—Flow diagram of radioactive solid waste-disposal system.

1. No oxides of nitrogen are produced by prolonged boiling of synthetic waste.
2. Oxides of nitrogen are released rapidly if the waste is made acidic.
3. No visible evolution of nitrogen dioxide

4. Off gas from the boiling (123°C) synthetic waste contains carbon dioxide much in excess of that present in air used to sparge the waste. Samples of concentrated sodium nitrate and sodium nitrite solutions have been irradiated to

$8 \times 10^9$  r to obtain information on the equilibrium point in the nitrate-nitrite conversion. Results indicate that the equilibrium concentration of nitrite ion is in excess of 4.4M when formed by radiolysis of 7.5M nitrate solutions.

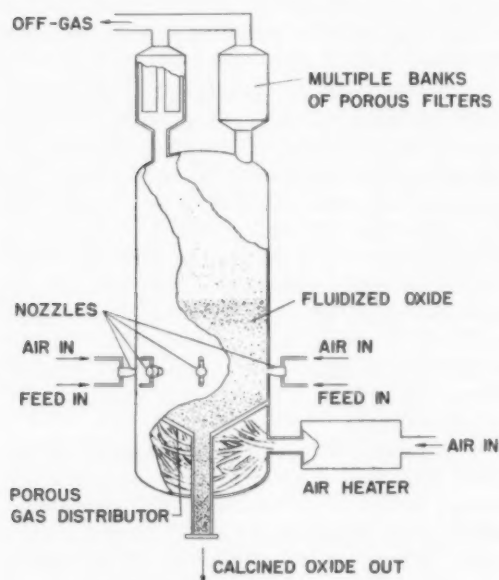


Fig. 13—Fluidized-bed calciner.

The future high-level waste-storage problem at Hanford has been reviewed. Expansion of facilities is expected to cost about 60 per cent more per gallon than the cost of the existing facilities. Purex tank farm costs are expected to be appreciably greater than this. Such costs encourage renewed research and development activities on alternate disposal methods. Methods of interest are (1) highly efficient separation and segregated dry storage for the long-lived fission products and (2) processing of wastes to achieve minimum volume for ultimate storage of mixed fission products.

Savannah River wastes are at present stored in tanks at the highest concentration that can be maintained at ambient temperature without precipitating solids. Consideration is being given to concentrating these wastes to higher solids content after a preliminary decay storage period. The concentrated waste would be stored in less expensive tankage.

In support of the Savannah River program, work at BNL<sup>5</sup> has included a study of (1) physical characteristics of both high- and low-level

wastes during storage, including sludge volumes, corrosion behavior, and possible heat and radiation instability problems, (2) problems to be encountered in the transfer of aged wastes, and (3) problems in the evaporation of wastes, such as scaling and foaming.

Simulated waste solutions (that are neutralized) were concentrated in a test tower using boil-up rates between 0.5 and 10 lb/(hr)(sq ft). No foaming was observed during concentration at these rates, and the decontamination factors (the ratio of solids in pot to overhead) were calculated at  $10^4$  to  $10^5$ . Corrosion studies on a number of systems have indicated that they can be held in 1020 mild steel. Experiments with a number of solutions containing sludges have indicated that they can be transferred effectively; however the inclusion of an agitation system prior to transfer is necessary. Agitation can be effected by recirculating the supernatant solution through a nozzle located in the sludge.

### *Converting Liquid Waste to Solid*

Radioactive wastes will have to be stored for long periods of time. Because a solid represents the minimum storage volume and because the storage of a solid seems intrinsically safer than that of a liquid, considerable effort is being put on methods of converting liquid wastes to solids. Methods considered have included (1) simple concentration until the liquid sets to a solid upon cooling, (2) the addition of Portland cement to form a mortar, (3) adsorption on clays or other naturally occurring materials, (4) fusion into ceramics or glasses, and (5) calcination.

As material becomes available, these various systems will be discussed under this section in subsequent reports. In this issue mention will be made of the work being done on fluid-bed calcination of wastes at Idaho Chemical Processing Plant (ICPP) and at ANL.

This process consists in evaporation and calcination of waste solutions to a granular solid consisting of the oxides of the constituent cations in a fluidized bed. A pictorial representation of the fluidized-bed calciner is shown in Fig. 13. The calciner consists of a cylindrical vessel containing a bed of granular oxide supported on a porous, conical, sintered stainless-steel plate. Preheated air is passed through the plate to fluidize the bed, the entire mass behaving much like a vigorously boiling liquid.



Waste solution is injected into the bed through pneumatic spray nozzles spaced on the periphery of the reactor in a single horizontal plane. The fluidized bed is operated at temperatures ranging from 400 to 500°C by means of electric heaters mounted either internally or externally.

The reactor is run under a vacuum of 0.5 to 5 in. Hg, supplied, by means of a steam jet exhauster, through multiple banks of porous, sintered stainless-steel filters. These filters are mounted in the top of the reactor to remove entrained oxide particles of greater than 2 to 3 $\mu$ . Five filter banks of two filters each are used and are manifolded such that blowback of one or more sets of filters may be accomplished simultaneously with off-gas removal through the other filter sets. Particulate removal may also be accomplished by directing the off-gas into cyclone separators and returning the collected fines to the reactor. The granular product is removed to storage containers by means of a bottom outlet or by means of an overflow pipe.

The volume reduction in converting the nitrate, primarily 2.3M Al(NO<sub>3</sub>)<sub>3</sub>, to the oxide is found to range from 6 to 10, the variation being due to variations in the bulk density of the oxide from run to run. The average bulk density is found to be approximately 0.77 g/cm<sup>3</sup>. The residual nitrate content of the oxide ranges from 2 per cent at a calcination temperature of 320°C to 0.2 per cent at 500°C.

A number of runs have been made in this unit using radioactive aluminum waste solutions (250 volumes of synthetic waste to 1 part ICPP waste). Less than 0.1 per cent of the feed activity other than ruthenium appears in the overhead condensate. The behavior of ruthenium appears to be a function of the operating temperature in the calciner. At 350°C, nearly 100 per cent of the ruthenium appears in the condensate; at 500°C, only 3 per cent comes overhead. The use of a mixture of carbon monoxide and nitrogen as the fluidizing gas at 400°C reduced the ruthenium in the condensate from 50 to 1 per cent.

### *Separation of Specific Isotopes*

There is interest in separating specific isotopes from waste streams for two reasons: (1) to remove long-lived isotopes quantitatively so that the remainder may be more easily bled off into the environment and (2) to provide radiation

sources of high specific activity and reasonable half life. Most interest centers around Sr<sup>90</sup> (for reason 1) and Cs<sup>137</sup> (for both reasons); some other isotopes are of marginal interest. Most of the recently published work is on cesium recovery.

Three methods for isolating cesium have been reported.<sup>6</sup>

1. Phenolic methylene sulfonic resins effectively removed the cesium from synthetic Redox waste solutions adjusted to a pH of 12 with sodium hydroxide. Flow rates between 1 and 2 ml/(min)(cm<sup>2</sup>) of resin-bed area were satisfactory, and more than 99 per cent of the cesium was removed from 50 resin-bed volume throughputs. This resin-bed capacity was, however, poorer than that found by other investigators, making a process based on this procedure economically marginal. The reason for this low resin capacity was probably due to the high salt content of the waste solutions.

2. Coformed nickel ferrocyanide (0.001M) was found to remove greater than 95 per cent of the cesium from tracer-level synthetic Redox waste solutions at pH values 0.5 to 2.5, giving a centrifuged slurry volume of from 4 to 6 per cent of the solution volume. The precipitate volume required to achieve greater than 99 per cent cesium removal was between 8 and 12 per cent of the total volume. In view of this high precipitate volume, the use of nickel ferrocyanide in removing cesium from Redox plant waste solution is also of doubtful economic value.

3. Zinc ferrocyanide was found to remove the cesium effectively from the tracer-level synthetic Redox waste solutions and from simulated full level solutions between pH values of -0.8 and 2.9. A threefold excess of ferricyanide was required to achieve greater than 95 per cent cesium removal when gross fission products were present. The centrifuged slurry volume was approximately 0.4 per cent of the solution volume.

A process for cesium isolation as the chloride from zinc-cesium ferricyanide precipitates was developed using barium hydroxide to free the cesium from tracer-level zinc ferricyanide precipitates.<sup>7</sup> Anion exchange was used to remove the ferricyanide, and the barium and trace zinc were precipitated with ammonium carbonate. The cesium was recovered as a cesium-potassium-sodium chloride mixture with a specific cesium gamma activity of about 19 curies/g.

This would constitute a satisfactory gamma-radiation source.

It has been shown<sup>8</sup> that a number of organophosphorus compounds and amines and thenoyl-trifluoroacetone were effective for extracting one or more of the long-lived fission products. Undiluted TBP, the most extensively studied reagent, extracted more than 99 per cent of the cerium, yttrium, zirconium, niobium, and ruthenium, although prior treatment was needed to convert the latter two elements to more extractable states. Strontium was extracted to a small degree, cesium not at all.

When a solid waste has been prepared, the leachability of that solid is of considerable interest. It may be desirable to leach off certain fission products from a mixed fission-product solid in order to make use of it, and in any event the long-term safety of the solid is affected by the degree of leachability. Considerable work is under way at various places and will be reported from time to time under this section. During this quarter a topical report on some Brookhaven work became available.<sup>9</sup>

Leaching experiments were carried out on alumina and mixtures of zirconia and alumina that contained quantities of inactive cesium, strontium, cerium, ruthenium, barium, yttrium, lanthanum, praseodymium, neodymium, and zirconium and were spiked with either  $\text{Sr}^{90}$  or  $\text{Cs}^{137}$ . Leaching was done at room temperature with a number of solutions including water and nitric acid at pH 4, 3, and 1. Some conclusions of the work are:

1. Nitric acid (pH 3) is an adequate leach for alumina to obtain a high percentage separation of both strontium and cesium and still maintain a low concentration of aluminum.

2. Nitric acid (pH 1) is adequate for the zirconia-alumina system to give a high percentage cesium separation and a low concentration of aluminum and zirconium. A continuous flow of large volumes of leach solution from a tank has little advantage over a system using much smaller volumes with agitation. The recovery of cesium and/or strontium by leaching is feasi-

ble. The leach will separate most of the cesium from either the alumina or zirconia-alumina along with varying amounts of strontium, which can then be further separated by ion-exchange techniques. The data indicate that after a fairly short period of time, in a matter of days, the leaching of oxides approaches a limiting value.

In this work the authors apparently mean 80 to 90 per cent by the term "high percentage separation." It should also be noted that in this work, only cesium or strontium was added as spike, and therefore data are not available on what other fission products would be leached off the calcined oxide.

## References

1. Symposium on the Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957, TID-7534, pp. 349-476. (Unclassified AEC report.)
2. Floyd P. Culler, Jr., and Stuart McLain, Status Report on the Disposal of Radioactive Waste, CF-57-3-114 (Rev.), June 25, 1957. (Unclassified AEC report.)
3. J. R. LaPointe, *Nucleonics*, 15(5): (May 1957).
4. V. R. Cooper, Monthly Report, July 1957, Chemical Research and Development Monthly Report [for] July 1957. (Secret AEC report.)
5. B. Manowitz, C. W. Pierce, and S. Zwickler, Studies on Characteristics of Savannah River Wastes, BNL-446, April 1957. (Unclassified AEC report.)
6. C. A. Goodall, HW-49658, Apr. 15, 1957. (Confidential AEC report.)
7. J. L. Hepworth, E. D. McClanahan, Jr., and R. L. Moore, Cesium Packaging Studies: Conversion of Cesium Zinc Ferrocyanide to a Cesium Chloride Product, HW-48832, June 1957. (Unclassified AEC report.)
8. H. L. Krieger, B. Kahn, and C. P. Straub, Removal of Fission Products from Reactor Wastes: Laboratory Studies of Liquid-Liquid Extraction from an Acid Aluminum Nitrate Solution, ORNL-2297. (Unclassified AEC report.)
9. A. Abrias, J. J. Reilly, and E. J. Tuthill, Separation of Cesium and Strontium from Calcined Metal Oxides as a Process in Disposal of High-level Wastes, BNL-453. (Unclassified AEC report.)

## CONVERSION TO FINAL PRODUCT OPERATIONS

After separation and decontamination the fissionable and fertile elements from spent nuclear fuels must be converted into reusable form. Purified uranium and plutonium from solvent-extraction operations are usually converted from the nitrate solutions into oxides, then into fluorides, and finally into metal or, in the case of uranium requiring reenrichment, into uranium hexafluoride. Developments in this area are summarized in the following paragraphs.

### *Continuous Production of $UO_3$*

Two processes are under development for the continuous conversion of recovered and decontaminated uranyl nitrate solution to uranium trioxide. One method employs an agitated trough calciner, and the other employs a fluidized-bed calciner. In both methods heat is transferred from external electrical heaters through the walls of the reactor to a bed of uranium trioxide which acts as a reservoir to supply heat for the denitration. Concentrated uranyl nitrate solution is continuously fed to the hot agitated uranium trioxide bed, resulting in thermal decomposition of the uranyl nitrate. By proper balance of the heating and feed addition rates, the bed is maintained at a predetermined temperature, around 300°C, which effects almost complete removal of nitrate and water from the oxide.

In the trough calciner under development at Hanford,<sup>1</sup> agitation of the bed is provided by means of a scraper-blade type agitator revolving at 74 to 80 rpm. Feed is introduced through injection tubes immersed below the bed level. Removal of dust from the off gas is achieved by means of a stainless-steel cloth filter with provision for blowback. The calcination process was recently demonstrated in a test program in which 200,000 lb of uranium trioxide was produced in a pilot-scale calciner 16 in. in diameter and 8 ft long. Satisfactory operation was achieved at oxide production rates up to 800 lb/hr.

In the fluidized-bed calciner, similar to that shown in Fig. 13, the energy for agitation is provided by the fluidizing air and decomposition gases rising through the bed.<sup>2</sup> Feed is injected through pneumatic spray nozzles mounted in the reactor wall below the bed level. Dust is separated by sintered stainless-steel filters and returned to the bed by reverse gas flow. This technique was demonstrated in a 6-in.-diameter reactor having a fluidized-bed depth of about 20 in. Several tons of uranium trioxide was produced in the development program at production rates of about 20 lb/hr.

The uranium trioxide produced by both methods is a relatively dense free-flowing material, consisting of nearly spherical particles. The oxide has a layered structure caused by successive depositions of uranium trioxide on the particle surface. The particle size ranges from about 20 to 325 mesh.

### *Fluidized-bed Production of $UO_2$*

In the existing facilities for the preparation of cascade feed uranium hexafluoride and the production of normal uranium metal, vibrating tray or screw reactors are employed for the reduction of uranium trioxide to uranium dioxide. Owing to the poor heat-transfer characteristics of this equipment, local overheating of the oxide accompanied by a significant decrease in chemical reactivity occurs. Loss in reactivity results in lower capacities in the subsequent hydrofluorination lines.

Bench-scale studies<sup>3</sup> disclosed that, when the reduction was carried out in a fluidized bed, the heat released could be dissipated rapidly enough to permit accurate temperature control, thus minimizing the reactivity loss. This has been confirmed by pilot- and plant-scale studies recently made at the Oak Ridge Gaseous Diffusion Plant.<sup>4</sup>

In the pilot-scale experiments using a 6-in. diameter two-stage reactor, conversions to uranium dioxide of greater than 97 per cent were consistently obtained during 1200 hr operation



at feed rates of about 60 lb of uranium trioxide per hour per cubic foot of bed and a bed temperature of 565°C. Evaluation of the product by hydrofluorination tests in a vibrating-tray pilot plant showed that the hydrofluorination rate with the fluid-bed reduced material was two to three times greater than that obtained with tray-reduced oxide. Ninety per cent conversion to uranium tetrafluoride was reached in one-half to one-third the time required with tray-reduced oxide.

In general, the plant studies verified the pilot-plant data.

In the pilot-plant studies it was found that partial reoxidation of the uranium dioxide significantly increased the reactivity of some oxides. With uranium trioxide produced in the Hanford continuous calciner, about 3 per cent reoxidation of the fluid-bed reduced material approximately doubled the hydrofluorination rate. The combined fluidized-bed reduction and reoxidation treatments increased the hydrofluorination line capacity to about four times the rate obtained with tray-reduced oxide.

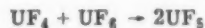
### *Oxidation of $UF_4$ to $UF_6$*

The reaction of uranium tetrafluoride with air or oxygen at high temperatures is potentially capable of producing uranium hexafluoride without the use of expensive fluorine gas. Uranyl fluoride is a product of the reaction, and this compound requires recycling after reconversion to uranium tetrafluoride by reaction with reducing agents and hydrogen fluoride. The process is currently being studied in bench-scale equipment.<sup>5-7</sup>

Initial attempts to carry out the reaction in a 4-in.-diameter moving-pellet reactor, to which heat was supplied by combustion of graphite pellets added to the uranium tetrafluoride pellets, resulted in local overheating with extensive fusion and bridging. A fluidized-bed reactor was then constructed and tested in batch oxidation runs at temperatures near 700°C. The extent of reaction was judged by the degree of conversion of uranium tetrafluoride to uranyl fluoride rather than by collection of the hexafluoride. Reaction rate constants of 0.58 to 0.76 reciprocal hours were obtained for the pseudo-first-order reaction at 730°C.

A brown-colored substance was swept out of the reactor along with the uranium hexafluoride.

This material was believed to have formed by volatilization of uranium pentafluoride from the reactor followed by disproportionation to various solid intermediates in the off-gas piping. The pentafluoride probably formed by the side reaction



Laboratory kinetic data showed that about 10 per cent of the uranium tetrafluoride was consumed by a side reaction at 700°C and about 30 per cent at 800°C.

In addition to the fluidized-bed reactor, a flame reactor has been constructed and is being installed for studying the oxidation process. Heat will be supplied to the uranium tetrafluoride particles by a carbon monoxide-oxygen flame.

### *Preparation of Metal*

The preparation of plutonium metal from Pu(IV) fluoride was recently described by Harmon.<sup>8</sup> Calcium metal is used as reductant, with iodine added as a booster to provide added heat. Reduction is carried out in a refractory-lined sealed container heated by induction or resistance furnaces. The booster reaction starts at about 400°C, whereas a temperature of over 600°C is necessary to initiate the calcium-plutonium fluoride reaction. Metal reduction yields of 97 to 99 per cent may be obtained in this process.

Uranium metal is produced in a similar manner by reduction of uranium tetrafluoride with magnesium metal, as described by Wilhelm.<sup>9</sup> Sealed containers lined with powdered magnesium fluoride slag are used, and the initiating temperature is in the range of 550 to 700°C. Recently a preliminary estimate was made of the cost of reducing uranium trioxide to metal by an electroreduction method similar to the Hall process for aluminum. Based upon a rate of 10 tons/day of metal, operating costs of \$0.332 and a mortization (5 years) costs of \$0.195/lb of uranium were found.<sup>10</sup> Laboratory studies have demonstrated the general feasibility of the process. Reduction efficiencies of 60 to 70 per cent were obtained regularly, and consolidated masses of metal product were produced in the laboratory cells.

### References

1. R. G. Geier, Continuous Calcination Equipment for Converting UNH to  $UO_3$ , HW-49652A, Apr. 2, 1957. (Unclassified AEC report.)
2. A. A. Jonke, E. J. Petkus, J. W. Loeding, and S. Lawroski, *Nuclear Science and Engineering*, 2: 303 (May 1957).
3. N. M. Levitz, E. J. Petkus, H. M. Katz, and A. A. Jonke, *Chemical Engineering Progress*, 53: 199 (April 1957).
4. D. C. Brater, C. C. Littlefield, J. H. Pashley, and S. H. Smiley, K-1329, Aug. 20, 1957. (Confidential AEC report.)
5. Chemical Technology Division Monthly Progress Report for March 1957, ORNL-2307, Aug. 12, 1957, p. 10. (Confidential AEC report.)
6. Chemical Technology Division Monthly Progress Report for April, 1957, ORNL-2324, Aug. 12, 1957, p. 8. (Confidential AEC report.)
7. Chemical Technology Division Monthly Progress Report for May, 1957, ORNL-2361, Sept. 27, 1957, p. 11. (Confidential AEC report.)
8. K. M. Harmon and W. H. Reas, in TID-7534, Symposium on the Reprocessing of Irradiated Fuel, Brussels, Belgium, May 20-25, 1957, p. 332. (Unclassified AEC report.)
9. H. A. Wilhelm, Volume 8, p. 162, Proceeding of the International Conference in Geneva, August 1955. (Available from International Documents Service, Columbia University Press, 2960 Broadway, New York 27, N. Y.)
10. L. W. Niedrach and A. C. Schafer, Electrowinning of Uranium from Its Oxides. II. A Preliminary Engineering Evaluation, KAPL-1668, Apr. 3, 1957. (Unclassified AEC report.)

# appendix

## Papers Presented at the Symposium for Reprocessing of Irradiated Fuels, Brussels, Belgium, May 20-25, 1957

### BOOK 1

#### SESSION I: AQUEOUS REPROCESSING

- Aqueous Reprocessing—An Introduction  
R. B. Richards  
Dissolution and Feed Adjustment  
R. E. Blanco  
Redox Process—A Solvent Extraction Reprocessing  
Method for Irradiated Uranium  
S. Lawroski et al.  
Application of the Packed Column to the Redox Process  
E. R. Irish  
The Purex Process—A Solvent Extraction Reproc-  
essing Method for Irradiated Uranium  
E. R. Irish et al.  
Application of the Pulse Column to the Purex Process  
R. G. Geier  
The Application of Mixer-Settlers to the Purex  
Process  
J. K. Davidson et al.  
Solvent Extraction Processes for Enriched Uranium  
C. E. Stevenson  
The Thorex Process  
F. R. Bruce

#### SESSION II: AUXILIARY PROCESSES

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less Steel  
C. M. Slansky  
Alternate Processing Methods for Zirconium and  
Stainless Steel Containing Fuels  
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Removal of Fission Products from Feeds  
Merle K. Harmon  
Tail End Treatment for Zirconium-Niobium Removal  
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Continuous Calcination Equipment for Converting UNH  
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Conversion Chemistry of Plutonium Nitrate  
K. M. Harmon et al.

#### SESSION III: DISPOSAL OF PLANT EFFLUENTS

- Effluent Disposal Considerations and Summary of  
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C. E. Stevenson  
Treatment of Gaseous Effluents  
Walter C. Schmidt  
Preparation of Waste for Liquid Disposal  
J. W. Ullmann  
The Retention of High Level Radioactive Wastes  
A. M. Platt  
Ultimate Disposal of Radioactive Wastes  
W. A. Rodger et al.  
Unit Costs and Economic Relationships for Certain  
Radioactive Waste Disposal Steps  
F. L. Culler et al.

### BOOK 2

#### SESSION IV: NON-AQUEOUS PROCESSING

- Non-Aqueous Processing—An Introduction  
S. Lawroski  
Fluoride Volatility Processes for Low Alloy Fuels  
R. C. Vogel et al.  
Fluoride Volatility Process for High Alloy Fuels  
G. I. Cathers  
Engineering and Economic Considerations of Volatility  
Processes; Part I—Engineering  
R. W. Kessie et al.  
Part II—Economics  
O. J. DuTemple et al.  
The Chemistry of Pyrometallurgical Processes: A  
Review  
Harold M. Feder  
Pyrometallurgical Processes: Process and Equip-  
ment Development  
E. Motta et al.  
Pyrometallurgical Processing: Economics and Pro-  
posed Engineering Applications  
J. H. Schraidt et al.

### BOOK 3

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F. L. Culler et al.

## Design for Criticality Control

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## Auxiliary Radiochemical Equipment

W. E. Unger

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## Operating Experience at Several Existing U. S. Nuclear Fuel Processing Plants

J. L. Schwennesen

## Radiation Exposure and Safety Experience in Radio-

## chemical Plants

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## Radiochemical Separations Processes: Chemical Safety

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## Heavy Element Isotopic Buildup

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## General Economics of Chemical Reprocessing for Solvent Extraction Processing

F. L. Culler

## Effect of Fuel Composition on Reprocessing Economics

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## Capital and Operating Cost Information on Several Existing U. S. Nuclear Fuel Processing Plants

J. L. Schwennesen

## Atomic Energy Commission Charges for Chemical Reprocessing Services

Myron B. Kratzer

## Notice of AEC Services in Chemical Processing of Spent Reactor Fuels







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